86-06459/

NATIONAL RESEARCH COUNCIL OF CANADA
NRCC ASSOCIATE COMMITTEE ON SCIENTIFIC CRITERIA
FOR ENVIRONMENTAL QUALITY

ALUMINUM IN THE CANADIAN ENVIRONMENT

Edited by Magda Havas and J.F. Jaworski

Subcommittee on Heavy Metals
and Certain Other Elements

Publication No. NRCC 24759
of the
Environmental Secretariat

Crown Copyright Reserved
1986

Available through prepaid orders only from:

Publications, NRCC/CNRC
Ottawa, Canada K1A 0R6

Price: $8.00

MANDATE OF THE ASSOCIATE COMMITTEE ON SCIENTIFIC CRITERIA FOR ENVIRONMENTAL QUALITY

The Associate Committee on Scientific Criteria for Environmental Quality was established by the National Research Council of Canada in response to a mandate provided by the Federal Government to develop scientific guidelines for defining the quality of the environment. The concern of the NRCC Associate Committee is strictly with scientific criteria. Pollution standards and objectives are the responsibility of the regulatory authorities and are set for the purpose of pollution control. These may be based on scientific criteria as a starting point but they also take into account the optimal socioeconomic impact of proposed measures as well as the state of existing technology.

The Associate Committee's program includes the evaluation of available information on the probability of effects of contaminants on receptors together with the related fundamental principles and scientific knowledge. In this work particular attention is directed to receptors and contaminants (and their interactions) important to Canada. This Canadian approach is necessary because evaluations made in other countries or regions will not always be applicable to the particular circumstances prevailing in Canada.

Members of the Associate Committee, its Subcommittees and Expert Panels, serve voluntarily and are selected for their individual competence and relevant experience with due consideration for a balance among all sectors in Canada. Responsibility for the quality of study documents rests with the Associate Committee. Each report is carefully reviewed according to a multistage procedure established and monitored by the National Research Council of Canada in order to preserve objectivity in presentation of the scientific knowledge. Publication and distribution of the report are undertaken only after completion of this review process.

Comments on Associate Committee documents are welcome and will be carefully reviewed by the Expert Panels. It is foreseen that these scientific criteria may be revised from time to time, as new knowledge becomes available.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the valuable review comments of P.G.C. Campbell, D.W. Schindler, E. Nieboer, K.L. Fischer, and G. Cowper.

ABSTRACT

Renewed interest in the toxicity of aluminum can be attributed both to its harmful effects on aquatic organisms and terrestrial plants at concentrations known to occur in some acidified waters and soils, and to its implication as a pathogenic factor in several human diseases, in particular Alzheimer's disease.

This document, which is divided into seven chapters, discusses the geochemistry of aluminum, including factors affecting aluminum speciation and mobility, and adsorption reactions involving aluminum; the aluminum chemistry of inland waters, including aluminum speciation and behavior of aluminum in streams and lakes; the effects of aluminum on aquatic biota, ranging from aquatic mosses to amphibians; aluminum in terrestrial ecosystems, including aluminum availability in soils and its effects on plants and microorganisms; aluminum in human health, focussing on human diseases associated with aluminum, such as osteodystrophy, dialysis encephalopathy, and senile and presenile dementia; aluminum in human diet; and the determination of aluminum in environmental samples, using such measurement techniques as atomic absorption and atomic emission spectroscopy.

Gaps in available information are identified, and recommendations are made for further research in such areas as biochemical responses to aluminum, the importance of aluminum in forest decline, and the determination of aluminum speciation in aqueous solutions.

RÉSUMÉ

Deux raisons expliquent le regain d'intérêt actuel à l'égard de la toxicité de l'aluminium. Premièrement, cet élément a des effets nuisibles sur les organismes aquatiques et sur les plantes terrestres à des concentrations observées dans certains plans d'eau ou dans certains sols acidifiés. Deuxièmement, on attribue à cet élément un rôle étiologique dans plusieurs maladies humaines, dont la maladie d'Alzheimer.

Les sept chapitres du présent document traitent des questions suivantes: la géochimie de l'aluminium, en particulier les facteurs qui influent sur la formation de ses dérivés, sur sa mobilité et sur les réactions d'adsorption auxquelles il participe; la chimie de l'aluminium dans les eaux intérieures, notamment la formation des ses dérivés et son devenir dans le cours d'eau et les lacs; les effets de l'aluminium sur le biote aquatique, depuis les mousses aquatiques jusqu'aux amphibiens; l'aluminium dans les écosystèmes terrestres, entre autres, sa disponibilté dans les sols et ses effets sur les plantes et les microorganismes; l'aluminium et la santé humaine, mais surtout les maladies humaines qui lui sont liées, comme l'ostéodystrophie, l'encéphalopathie démentielle des hémodialysés et les démences sénile et présénile; l'aluminium dans l'alimentation humaine; et enfin, le dosage de l'aluminium à l'aide de techniques spectroscopiques d'absorption et d'émission atomiques.

On signalé des lacunes dans les connaissances actuelles et l'on recommande de pousser plus loin les recherches concernant les réactions biochimiques dans lesquelles intervient l'aluminium, le rôle de l'aluminium dans le dépérissement des forêts et le dosage des dérivés de l'aluminium en solution aqueuse.

SUMMARY

Aluminum (Al) is the 13th element in the periodic table. It has an atomic weight of 26.9815, an atomic radius of 0.1432 nm, and electron negativity of 1.5. It has one stable isotope (^{27}Al) and one naturally occurring radioisotope (^{26}Al, $t_{1/2} = 7.4 \times 10^5$ a).

Aluminum is the third most abundant element (after oxygen and silicon) in the lithosphere, and comprises approximately 8% by weight of the earth's crust. It is found in igneous rocks (especially feldspar), hydrothermal deposits (zeolite, cryolite), and sedimentary rock (particularly clays such as kaolinite). Concentrations of aluminum in rocks range from 9000 $\mu g \cdot g^{-1}$ (limestone) to 88 000 $\mu g \cdot g^{-1}$ (shale). Concentrations of aluminum in soils range from 10 000 to 300 000 $\mu g \cdot g^{-1}$. Aluminum does not occur as a free metal in nature. Bauxite and, to a lesser extent, cryolite are the important ores for the production of purified alumina (Al_2O_3).

Aluminum is an important element in the crystal structure of certain soil minerals. Most of this aluminum is tightly bound in an oxygen-containing silicate lattice, and weathers slowly. Concentrations of aluminum in soil water, in groundwater, and in surface water are generally quite low relative to the vast amounts and high concentrations in surrounding soils and rocks. Weathering and leaching rates of aluminum can be increased by acidification. This can occur as a result of acidic deposition caused by man-made emissions of sulfur dioxide and nitrogen oxides, or as a result of natural production of organic and mineral acids. In temperate, boreal regions with podsolic soils, aluminum is leached from the A horizon, and is deposited along with iron and certain trace metals in the lower B horizon. This contrasts with the humid tropics, where silicates are leached downward during the process of laterization, leaving behind sesquioxides of iron and aluminum. In spite of the high concentrations of aluminum in many soils, most of the aluminum is tightly bound and not readily available to plant roots. Only under acidic or very alkaline conditions does this aluminum become available.

Aluminum occurs in a particulate form in the atmosphere, being derived from wind-blown soil and particulate emissions from smelters and coal-fired power plants. Concentrations of aluminum deposited from the atmosphere (wet and dry fallout) vary considerably, but are generally less than 0.16 $mg \cdot L^{-1}$.

Concentrations of aluminum in fresh water are generally less than 0.02 $mg \cdot L^{-1}$, but they can be greatly elevated (to more than 1 $mg \cdot L^{-1}$) in situations where acid leaching of aluminum from soils occurs. The solubility of aluminum is pH-dependent, with relatively low solubility between pH 5.5 and 7.0, and increasing solubility at lower and higher pH values; for example, below pH 4, the concentration of aluminum may exceed 100 $mg \cdot L^{-1}$. Although pH is one of the most important factors affecting the solubility and speciation of aluminum, organic ligands, fluoride, sulfate, phosphate, silicates, and suspended solids can all bind with aluminum and thus change its chemical form, solubility, and bioavailability.

Concentrations of aluminum in biota tend to be highly variable. Values may be as low as 0.1 $\mu g \cdot g^{-1}$ in some herbaceous plant species, and as high as 6000 $\mu g \cdot g^{-1}$ in others (certain lichens and bryophytes). There are a few aluminum accumulators, such as tea (Camellia sinensis), that may have concentrations of aluminum as high as 30 000 $\mu g \cdot g^{-1}$ in foliage. Aluminum generally does not appear to be an essential nutrient in either plants or animals. However, a few plant species that normally grow on soils with high aluminum availability are more productive in the presence of small quantities of aluminum in controlled culture solutions.

Early studies reported that plant growth was poor in acidic soils and attributed this partly to high concentrations of available aluminum (although availability of other potentially toxic metals was also high). The aluminum interfered with root growth and with uptake of phosphate from the soil. Recent studies have reported very high concentrations of aluminum in the nuclei of dividing cells in the root tip. Both liming and fertilizing with phosphorus reduced aluminum toxicity in agricultural crops, probably because of decreased solubility and chemical precipitation of aluminum.

Recent reports of forest decline, particularly in Germany, suggest that aluminum may be one of several factors responsible for this decline. Damage to trees was noticed after two particularly dry years. Drought favors the chemical oxidation of sulfur and ammonium; this increases acidity which in turn favors the dissolution of aluminum. High concentrations of aluminum were found in the soil solutions, and roots showed symptoms resembling aluminum toxicity.

The symptoms of aluminum toxicity in plants resemble those associated with toxicity of other metals and/or phosphorus deficiency. These include inhibition of root elongation, dwarfing, browning of root tip, and lack of fine root branching. The roots become inefficient at extracting water and nutrients from the soil. Above-ground symptoms include stunting, reduced yield, small dark green foliage, delayed maturity, purple-tingeing of various tissues, and yellowing or necrosis of leaf tips.

Whereas most plants are sensitive to aluminum, a few are aluminum-tolerant. There is some evidence that tolerant varieties have a relatively low root surface cation-exchange capacity, and that they decrease rather than increase the acidity of the rhizosphere. There is also evidence that aluminum tolerance is a heritable trait in some plants.

Aluminum may interfere with phosphorus uptake in aquatic plants, just as it does in terrestrial plants. Studies with algae have shown that phosphorus uptake and photosynthetic ^{14}C uptake are reduced in the presence of high concentrations of aluminum.

Concentrations of aluminum below 0.2 $mg \cdot L^{-1}$ in water can be toxic to some aquatic animals in oligotrophic lakes. Aluminum interferes with respiration, sodium and chloride regulation, and possibly calcium uptake in some species. Fish kills in Scandinavia and the failure of some restocking programs in the United States have been attributed to high concentrations of aluminum in water. In fish, maximum aluminum toxicity occurs around pH 5.5; in Cladocera, it occurs at slightly higher pH (pH 6.5). At lower pH (less than pH 4.5), aluminum can actually be beneficial to aquatic animals. Organic ligands (e.g. citrate) and, to a lesser extent, inorganic ligands (e.g. fluoride), as well as calcium, can reduce the toxicity of aluminum to aquatic biota.

High concentrations of aluminum have been found in the gills of fish living in aluminum-contaminated water. It is believed that particulate aluminum on the gills is adsorbed to the mucus and physically interferes with respiration. The liming of acidic lakes that have high concentrations of aluminum can be devastating to indigenous fish populations because of this clogging of gills.

Brook trout, rainbow trout, and brown trout are moderately aluminum-sensitive, as are some cladoceran crustaceans. On the other hand, aquatic insects, particularly chironomids, Chaoborus spp., dytisid beetles, and caddisflies, are moderately aluminum-tolerant, and occur in acidic, aluminum-contaminated water. High concentrations of aluminum in insects emerging from acidic, aluminum-contaminated lakes are believed to contribute to reproductive impairment in pied flycatchers in Sweden, via thinning.

North Americans ingest an average of approximately 36 mg of aluminum per day. However, individual intakes vary greatly, depending on the type of food consumed. Drinking water in some communities may have high concentrations of aluminum because of natural sources or the purification process which may involve addition of alum ($K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$). Processed cheese and pickled vegetables contain high concentrations of aluminum, as do some common drugs such as buffered aspirin and certain antacid tablets and antidiarrheals. Cooking salty, acidic, or alkaline food in aluminum cookware and storing food in aluminum foil can increase the aluminum concentration. Although ingestion is the major route of aluminum intake, it is reassuring to know that very little aluminum is absorbed through the gut. In healthy humans, fecal and urinary excretion approximately equals uptake.

ALUMINUM IN THE CANADIAN ENVIRONMENT

EDITED BY

MAGDA HAVAS AND J.F. JAWORSKI

NRCC No. 24759

The total body burden of aluminum in a normal individual is approximately 30 mg. Aluminum concentrations in serum and in tissue, with the exception of the lung, are quite low (0.005 and 1.5 $mg \cdot L^{-1}$, respectively). Therefore, under average conditions of exposure, the skin, lung, and gastrointestinal tract are effective barriers to aluminum.

The uptake, retention, and distribution of aluminum can be altered by several factors. The pH of the environment influences availability; free aluminum is 2 to 3 orders of magnitude higher at pH 4 than at pH 6.2. This suggests that gastrointestinal absorption of aluminum must occur in the acidic environment of the stomach and duodenum. Aluminum retention and distribution vary greatly with the type of aluminum salt (aluminum phosphate, aluminum hydroxides, aluminum carbonates) ingested. An increase in parathyroid hormone (PTH) increases the absorption and retention of orally ingested aluminum in rats.

Aluminum in plasma is either bound to proteins or present as free unbound aluminum. Once the plasma proteins are saturated with aluminum, there is an increase in unbound filterable aluminum, as well as in urinary excretion of aluminum. Presumably, unbound filterable aluminum species have access to extracellular and intracellular compartments.

The actions of aluminum at the cellular level include:

(i) nuclear effects such as binding to DNA phosphate and bases, blockage of initiation sites for RNA polymerase, blockage of ADP ribosylation, alteration of sister chromatid exchange, alteration of steroid-induced chromosome puffing, and inhibition of corticosterone receptor binding to DNA;

(ii) cytoplasmic effects such as blockage of calmodulin-dependent Ca/Mg-ATPase which is important in the extrusion of calcium from cells, inhibition of hexokinase, and stabilization of the terminal phosphoryl group on ATP;

(iii) membrane effects such as alteration of physical properties of membrane lipids, blockage of high affinity uptake of GABA and glutamate from synaptosomes, inhibition of acetylcholinesterase, alteration of adenyl cyclase activity, enhancement of brain-specific lipid peroxidation, and blockage of calcium uptake; and

(iv) blood effects such as alteration of activity of cholinesterase and interactions with transferrin.

High concentrations of aluminum in humans have been associated with several illnesses. Lung diseases such as pulmonary fibrosis and emphysema have been reported among workers exposed to high levels of finely powdered aluminum metal. Bladder cancer has also been reported in workers exposed to aluminum emissions, particularly in smokers. Fatal encephalopathy was reported for patients on dialysis for chronic renal failure. Two types of bone disease are associated with aluminum: hypophosphatemic osteomalacia, which is an indirect effect of systemic aluminum exposure and is unrelated to dialysis encephalopathy syndrome

(DES), and osteomalacic renal osteodystrophy, which appears to be a direct manifestation of aluminum toxicity and is an important consideration in all cases of renal failure. Severe anemia preceding the encephalopathic and osteomalacic symptoms of DES has been reported in patients with extremely high (0.55 $mg \cdot L^{-1}$) serum aluminum concentrations. It is believed that aluminum interferes with hemoglobin synthesis. Gastrointestinal disturbances, including anorexia, vomiting, and weight loss, have been described in several reports of DES. In normal humans, the constipating effect of aluminum-containing antacids is well known. Sudden cardiac death has been reported in some patients suffering from DES. It is believed that depletion of myocardial magnesium by aluminum was responsible for the cardiac arrest. High levels of aluminum in DES can thus exert a cardiotoxic effect. High concentrations of aluminum in hepatocytes and severe lesions in hepatic cells (hepatotoxicity) have been found in a patient dying of DES.

Perhaps one of the most feared diseases associated with aluminum is Alzheimer's disease, which accounts for approximately 60-70% of senile dementia cases, and is a major social and medical health problem throughout the world. High concentrations of aluminum have been found in brain tissue of patients who suffered from Alzheimer's disease. Aluminum is considered to be involved in the pathogenesis of the disease, rather than the etiology. However, the exact role aluminum plays in this disease is not known.

Although it has been shown that normal healthy humans do not accumulate aluminum readily from the environment, some high-risk groups are vulnerable when exposed to elevated concentrations of aluminum in air, food, or water. Whereas it is known, for example, that exposure to high concentrations of aluminum in air increases the probability of pulmonary fibrosis, it is not known whether exposure to high concentrations of aluminum in food or drinking water has a similar, potentially causal effect for some of the neurological diseases. Nor is it known whether removal of aluminum from the body alters the course of the disease in people at risk. Aluminum can be toxic to humans, although its exact role in human diseases needs more research.

A number of techniques are available for the determination of aluminum in environmental samples, although great care must be taken to reduce contamination. Aluminum is ubiquitous, and can be found in glassware, plastic bottles, filters, and chemical reagents. The techniques for measuring total aluminum include atomic absorption spectroscopy, emission spectroscopy, visible spectrophotometry, fluorescence, and activation analysis. Different forms of aluminum can be determined with electrochemical methods such as pulse polarography, or after separation using gas chromatography or ion-exchange columns.

There are a number of methods for determining the aquatic speciation of aluminum. The major categories of aluminum species are defined in an operational/analytical sense and include total dissolved aluminum, mononuclear aluminum, polynuclear aluminum, and organic aluminum. Because about half of the total dissolved aluminum passes through a 0.45-µm filter, it is not clear whether samples should be filtered or what size filter should be used for the determination of total dissolved aluminum. Mononuclear aluminum is believed to consist of simple inorganic complexes and perhaps simple low-molecular-weight organic complexes. It has been called "fast-reactive" aluminum because of the method used. Polynuclear aluminum may be obtained by difference (total - mononuclear) and may include both organic and inorganic fractions. The difference between digested and nondigested samples gives polynuclear aluminum. Organically complexed aluminum is generally obtained by size exclusion, photolytic oxidation, or ion-exchange column. The difference in analysis of total aluminum before and after column treatment is reported as organically bound aluminum. All these techniques have their shortcomings, and studies are currently being performed in an attempt to improve them.

Aluminum species can also be predicted based on thermodynamic constants. Computer models have been designed to provide the dominant forms of aluminum in natural environments. The stability constants for many organic and inorganic aluminum complexes have been determined, although there is agreement for only a few of these. Also, reliable and complete environmental chemistry is required for these models to provide meaningful results.

RESEARCH RECOMMENDATIONS

1. Development of a recommended procedure for determining aluminum speciation in aqueous solutions (this should include interlaboratory comparisons to verify the methodology).

2. Improvement of input thermodynamic data for computer-assisted models used for calculating aqueous concentrations of aluminum species under different environmental conditions.

3. Investigation of abiotic factors (pH, calcium, phosphate, fluoride, organic ligands) affecting aluminum availability in soil and water as well as implications for the health of plants and animals.

4. Investigation of possible synergistic or antagonistic effects of other metals (e.g. iron, zinc, manganese, copper, nickel, cadmium) on aluminum toxicity.

5. Elucidation of the mechanisms of the physiological and biochemical responses of aquatic organisms to aluminum.

6. Studies on the effects of aluminum on indicator organisms as well as on sensitive life-cycle stages (germination, fertilization, hatching, molting, etc.).

7. Evaluation of the importance of aluminum in forest decline with emphasis on aluminum-drought interactions, aluminum-calcium interactions, and aluminum-pH interactions at the root surface.

8. Determination of whether exposure to aluminum of people at risk affects the progress of certain diseases.

9. Determination of whether removal of aluminum from affected individuals changes the course of these diseases.

10. Development of a cell model for aluminum interaction and transport.

TABLE OF CONTENTS

		PAGE
SUMMARY		5
RESEARCH RECOMMENDATIONS		11
LIST OF TABLES		17
LIST OF FIGURES		20
LIST OF APPENDICES		23
1.0	ALUMINUM GEOCHEMISTRY	25
	J.R. Kramer	
1.1	Previous Reviews	25
1.2	General Geochemical Setting	25
1.2.1	Aluminum in Rocks	25
1.2.2	Aluminum in Clays	26
1.2.2.1	Aluminum Mobilization from Clays	28
1.3	Factors Affecting Aluminum Speciation and Mobility	28
1.3.1	pH	29
1.3.1.1	pH and Aluminum Solubility	29
1.3.1.2	pH and Aluminum Hydrolysis	30
1.3.1.3	Kinetics	33
1.3.2	Organic Matter	34
1.3.3	Fluoride	34
1.3.4	Sulfate	37
1.4	Adsorption Reactions Involving Aluminum	37
1.4.1	Clays	37
1.4.2	Phosphate	41
1.4.3	Sulfate Sorption and Mineral Formation	41
1.5	Concentrations and Availability in Various Environments	42
1.5.1	Surface Waters, Groundwaters, and Soil Solutions	42
1.6	Methods for Aquatic Speciation of Aluminum	43
1.7	Aluminum Hydroxy Complexes	46
2.0	ALUMINUM CHEMISTRY OF INLAND WATERS	51
	Magda Havas	
2.1	Introduction	51
2.2	Sources of Aluminum	51
2.3	Aluminum Speciation	53
2.3.1	Aluminum Hydroxide Complexes	58
2.3.2	Aluminum Fluoride Complexes	58
2.3.3	Aluminum Sulfate Complexes	58
2.3.4	Aluminum Phosphate Complexes	58
2.3.5	Aluminum Organic Complexes	60
2.4	Aluminum in Streams	60
2.4.1	Concentrations	60
2.4.2	Speciation	61
2.4.3	Seasonal Changes in Aluminum	61
2.4.4	Changes in Aluminum Solubility	64
2.5	Aluminum in Lakes	64
2.6	Aluminum as a Buffer	67

TABLE OF CONTENTS (Cont'd)

PAGE

2.7 Aluminum Budget 69
2.8 Field Experiments 69
2.8.1 Acidification 69
2.8.2 Liming 71
2.8.3 Aluminum Additions 71
2.9 Acid Mine Drainage 75

3.0 EFFECTS OF ALUMINUM ON AQUATIC BIOTA 79
Magda Havas
3.1 Introduction 79
3.2 Aquatic Mosses and Macrophytes 79
3.3 Algae 84
3.3.1 Aluminum Content 84
3.3.2 Aluminum Toxicity 86
3.3.3 Algae in Acidic, Aluminum-contaminated Environments 87
3.3.4 Inducing Aluminum Tolerance 94
3.3.5 Aluminum as an Essential Micronutrient 95
3.4 Microcrustaceans 95
3.4.1 Distribution 95
3.4.2 Mortality and Reproduction 96
3.4.3 Aluminum Content 99
3.4.4 Physiological Responses 101
3.5 Crayfish 103
3.6 Insects 103
3.6.1 Distribution 103
3.6.2 Aluminum Toxicity 103
3.6.3 Aluminum Content 105
3.7 Rotifers 105
3.8 Fungi and Bacteria 106
3.9 Amphibians 106
3.10 Fish 108
3.10.1 Lethal Concentrations 108
3.10.2 Sublethal Symptoms and Concentrations 112
3.10.3 Physiological and Biochemical Responses 114
3.10.4 Species and Age-class Differences 117
3.10.5 Effects of Aluminum Speciation 120
3.10.6 Acclimation 122
3.11 Birds 126

4.0 ALUMINUM IN TERRESTRIAL ECOSYSTEMS 129
B. Freedman and T.C. Hutchinson
4.1 Introduction 129
4.2 Terrestrial Biogeochemistry of Aluminum 130
4.3 Aluminum Availability in Soils 134
4.4 Aluminum and Soil Acidity 139
4.5 Aluminum and Acidic Deposition 140
4.6 Aluminum Concentrations in Plants 143
4.7 Effects of Aluminum on Plants 146

TABLE OF CONTENTS (Cont'd)

PAGE

4.8 Aluminum Tolerance in Plants 147
4.9 Aluminum and Microorganisms 150
4.10 Summary and Conclusions 151

5.0 ALUMINUM IN HUMAN HEALTH 153
D.R. Crapper McLachlan and B.J. Farnell
5.1 Introduction 153
5.2 Aluminum Ingestion 153
5.3 Aluminum Metabolism 153
5.3.1 Absorption, Excretion, Transport 153
5.3.2 Cytotoxicity 158
5.4 Human Diseases Associated with Aluminum 158
5.4.1 Pulmonary Diseases 158
5.4.2 Osteodystrophy 158
5 4.3 Anemia 165
5.4.4 Gastrointestinal Toxicity 166
5.4.5 Cardiotoxicity 167
5.4.6 Hepatotoxicity 167
5.4.7 Granuloma Induction 167
5.4.8 Cancer 167
5.4.9 Dialysis Encephalopathy 168
5.4.10 Primary Degenerative Brain Disease: Senile and Presenile Dementia of the Alzheimer Type 169
5.4.10.1 Evidence Implicating Aluminum in Alzheimer's Disease 169
5.4.10.1.1 Aluminum Concentrations in Brain Tissue 169
5.4.10.1.2 Intracellular Distribution of Aluminum in Brain 171
5.4.10.1.3 Clinical Course of Alzheimer's Disease and Aluminum Encephalopathy 171
5.4.10.1.4 Affected Cell Populations and Neurofibrillary Degeneration 172
5.4.10.1.5 Reduced Choline Acetyl Transferase 172
5.4.10.1.6 Dialysis Encephalopathy vs. Alzheimer's Disease 172
5.4.11 Guam Parkinson-Dementia, Amyotrophic Lateral Sclerosis Complex 173

6.0 ALUMINUM IN THE HUMAN DIET 175
J.F. Jaworski
6.1 Natural Levels 175
6.2 Aluminum Additives 175
6.3 Estimated Daily Intake 175
6.4 Aluminum in Nonprescription Drugs 175
6.5 Aluminum Uptake 179
6.6 Aluminum Cookware and Foil Wrap 179

TABLE OF CONTENTS (Cont'd)

PAGE

7.0 THE DETERMINATION OF ALUMINUM IN ENVIRONMENTAL SAMPLES 181
J.F. Jaworski
7.1 Introduction 181
7.2 Possible Errors in Aluminum Analysis 181
7.2.1 Contamination 181
7.2.1.1 Contamination from Dust 181
7.2.1.2 Contamination of Laboratory Reagents 181
7.2.1.3 Contamination from Laboratory Apparatus Containing Aluminum 185
7.3 Sampling and Sample Storage 189
7.3.1 Aqueous Samples 189
7.3.2 Biological Samples 189
7.3.3 Geological Samples 189
7.4 Sample Treatment Prior to Analysis 189
7.5 Measurement Techniques 190
7.5.1 Atomic Absorption (AA) 190
7.5.1.1 Flame Atomization 190
7.5.1.2 Graphite Furnace Atomization 190
7.5.2 Atomic Emission Spectroscopy (AES) 191
7.5.2.1 Flame Emission 191
7.5.2.2 Furnace Emission 194
7.5.2.3 Inductively Coupled Plasma (ICP) Emission 194
7.5.2.4 Direct Current (DC) Plasma Arc Emission 194
7.5.2.5 Gas Chromatography/Emission Spectroscopy 194
7.5.2.6 Laser Probe/Emission Spectroscopy 199
7.5.3 Spectrophotometry 199
7.5.4 Fluorescence Methods 199
7.5.4.1 Fluorometry 199
7.5.4.2 Atomic Fluorescence Spectrometry 199
7.5.4.3 X-ray Fluorescence Spectrometry 202
7.5.4.4 Electron Spectroscopy for Chemical Analysis (ESCA) 202
7.5.5 Activation Analysis 202
7.5.5.1 Neutron Activation 203
7.5.5.2 Charged-particle Activation Analysis 203
7.5.6 Gas Chromatography (GC) 205
7.5.7 Electrochemical Methods 205
7.5.8 Mass Spectrometry 205
7.6 Standard Reference Materials (SRM) 207
7.7 Conclusion 207

REFERENCES 269

LIST OF TABLES

TABLE		PAGE
1-1	Surface-related characteristics of some clay minerals	27
1-2	Comparison of values of pK, at zero ionic strength, 25°C	32
1-3	Comparison between the dissociation constants and the complex formation constants of aluminum with some organic acids	35
2-1	Concentration of aluminum in precipitation and in suspended particulates	52
2-2	Aluminum concentrations in surface, ground, and interstitial water	54
2-3	Aluminum concentrations in stream water	55
2-4	Mean annual concentrations of Al, Zn, Mn, and Fe in Lake 223 during the first 3 years of acidification	70
2-5	Chemical changes associated with liming	73
3-1	Relative abundance of aquatic mosses and macrophytes in clear-water acidic environments (≤pH 5.6)	80
3-2	Aluminum concentrations in aquatic macrophytes	82
3-3	Concentrations of aluminum in aquatic macrophytes collected from lakes in south-central Ontario, fall, 1984	83
3-4	Aluminum concentrations in algae	85
3-5	Algae found in acidic, aluminum-contaminated water	88
3-6	Minimum pH and maximum aluminum concentrations at which crustaceans have been recorded in North America	97
3-7	Aluminum content of *Daphnia magna* at different pH levels and external aluminum concentrations	100

LIST OF TABLES (Cont'd)

TABLE		PAGE
3-8	Minimum pH and maximum aluminum concentrations at which insects have been recorded in North America	104
3-9	Minimum pH and maximum aluminum concentrations at which rotifers have been recorded in North America	107
3-10	Acute toxicity of aluminum to freshwater fishes in hard water	109
3-11	Acute toxicity of aluminum to freshwater fishes in soft water	111
3-12	Acute toxicity of aluminum to marine fishes	113
3-13	pH level necessary to prevent measurable (≥ 15%) reduction in survival of early life history stages of brook trout and white suckers assuming no aluminum or aluminum concentrations typical of an Adirondack surface water at that pH level	121
4-1	Concentrations of aluminum in a range of biogeochemical compartments	131
4-2	Fluxes of aluminum in a beech and a spruce forest in West Germany	132
4-3	Vertical distribution of total aluminum in some typical U.S. forest soils	135
4-4	Effect of liming on soil pH, KCl-extractable aluminum, and relative yield of barley	138
4-5	Selected examples of aluminum hyperaccumulators	144
4-6	The influence of soil pH and phosphorus fertilization on the aluminum concentrations in the above-ground tissues of *Pennisetum clandestinium*, an Australian pasture grass	145
5-1	Human conditions associated with elevated aluminum	154
5-2	Actions of aluminum at the cellular level	159
5-3	Comparison of characteristics of experimental aluminum encephalopathy and Alzheimer's disease	170

LIST OF TABLES (Cont'd)

TABLE		PAGE
6-1	Aluminum concentrations in different classes of food not containing aluminum as a food additive	176
6-2	Aluminum concentrations in fish and shellfish	177
6-3	Aluminum-containing food additives permitted in the U.S.A. and Canada	178
6-4	Nonprescription drugs that contain aluminum	180
7-1	Sources of aluminum contamination	182
7-2	Aluminum in some commercially available acids, distilled water, and ion-exchange resins	183
7-3	Aluminum concentrations in glass	184
7-4	Aluminum concentrations in plastic	186
7-5	Leaching of aluminum from the surface of plastic bottles	187
7-6	Aluminum concentrations in filtering media	188
7-7	Example of aluminum analyses performed using graphite furnace atomizers	193
7-8	Some interferences and matrix effects in plasma emission determination of aluminum	195
7-9	Aluminum signal enhancement by easily ionized elements in direct current plasmas	198
7-10	Spectrophotometric determination of aluminum	200
7-11	Fluorimetric determination of aluminum	201
7-12	Determination of aluminum using neutron activation analysis	204
7-13	Determination of aluminum using charged-particle activation analysis	206
7-14	Ion probe analysis for aluminum	208
7-15	Some examples of standard reference materials with a certified aluminum concentration	209

LIST OF FIGURES

FIGURE		PAGE
1-1	Predominance diagram for monomeric ($AlOH^{2+}$) and polynuclear ($Al_m(OH)_n$) species	31
1-2	Plot of stability constants of Al^{3+} and corresponding Fe^{3+} complexes	36
1-3	Predominate form of aluminum complex and ratio of free aluminum activity to total dissolved aluminum as a function of pH and fluoride activity	38
1-4	Predominate form of aluminum complex and ratio of free aluminum activity to total dissolved aluminum as a function of pH and sulfate activity	39
1-5	Predominate form of aluminum complex and ratio of free aluminum activity to total dissolved aluminum as a function of sulfate and fluoride activity at low pH	40
1-6	Schematic for aluminum speciation using Driscoll (1980) method	47
1-7	Schematic for aluminum speciation using LaZerte (1984) technique	48
1-8	Schematic for aluminum speciation using Campbell *et al.* (1983) method	49
2-1	Aluminum concentrations at different pH values in various bodies of water	56
2-2	Aluminum concentrations at different pH values in freshwater lakes in the Adirondacks, Sweden, Norway, and Scotland	57
2-3	Refound phosphorus after additions of 50-100 $\mu g \cdot L^{-1}$ ortho-P to Lake Horsikan water of pH 4.1 containing 0.5 $mg \cdot L^{-1}$ Al	59
2-4	Changes in the concentrations of (a) hydrogen ions and aluminum species, and (b) total and free fluoride downstream	62
2-5	Concentrations of organic and inorganic forms of aluminum downstream	63

LIST OF FIGURES (Cont'd)

FIGURE		PAGE
2-6	Seasonal changes in pH and aluminum in (a) Lake Horsikan and (b) Lake Rävekärr	65
2-7	Seasonal changes in pH, total organic carbon concentrations, and aluminum speciation in rivers (a) and lakes (b) in the Adirondack Mountains	66
2-8	Titration curve for (a) an acidic (pH 1.8), metal-contaminated pond in the Canadian Arctic, and (b) an acid strip mine lake	68
2-9	Seasonal changes in aluminum, calcium, dissolved organic carbon concentrations, pH, and stream discharge in Norris Brook, New Hampshire	72
2-10	Effect of liming on seasonal aluminum concentrations in stream water	74
2-11	Processes involved in acid strip mine lake recovery	77
3-1	Survival of *Daphnia magna* exposed to low pH and elevated concentrations of aluminum in water containing 2.5 and 12.5 mg·L^{-1} Ca	98
3-2	Calcium and aluminum contents of *Daphnia magna* as a function of pH and aluminum concentrations in the water	102
3-3	Ionic and covalent indices for metal ions	115
3-4	Plasma chloride concentrations in brown trout (*Salmo trutta*) exposed to different aluminum concentrations at pH 5.0	118
3-5	Plasma chloride concentrations in brown trout (*Salmo trutta*) exposed to pH 4.0 with and without aluminum	119
3-6	Effect of aluminum citrate, aluminum fluoride, and free aluminum on survival of brook trout (*Salvelinus fontinalis*) at different pH levels	123
3-7	Survival of aluminum-acclimated and nonacclimated brook trout (*Salvelinus fontinalis*) sac fry at pH 4.0 and 4.5 at elevated concentrations of aluminum	124

LIST OF FIGURES (Cont'd)

FIGURE		PAGE
3-8	Survival of aluminum-acclimated and nonacclimated brook trout (Salvelinus fontinalis) yearlings at pH 4.5 and 5.0 at elevated concentrations of aluminum	125
4-1	Solubility of aluminum in water as affected by pH	136
7-1	Standard curves showing the effects of different matrices on the aluminum signal	192
7-2	Influence of different metals on the ICP signal intensity from a 1 $mg \cdot L^{-1}$ Al solution	196
7-3	Effect of potassium (K^+) on the emission intensity of aluminum atoms at 396.2 nm	197

LIST OF APPENDICES

APPENDIX		PAGE
I.0	Aluminum Hydrolysis Review	211
II.0	Aluminum-Organic Speciation	219
III.0	Freshwater Aluminum Studies	263
IV.0	Abbreviations Used in the Text	267

1.0 ALUMINUM GEOCHEMISTRY

J.R. Kramer

Department of Geology
McMaster University
Hamilton, Ontario L8S 4M1

1.1 PREVIOUS REVIEWS

The literature on aluminum geochemistry research is extensive. Early work was reviewed by Hutchinson (1943); more recent reviews are by Sorenson et al. (1974), Burrows (1977), and Brusewitz (1984).

1.2 GENERAL GEOCHEMICAL SETTING

Aluminum is very abundant in the earth's crust (approximately 8% by weight). The atomic ratio of Al to Si is about 0.31. The solid-phase geochemistry of aluminum is mostly determined by its ionic radius, 0.057 nm, which enables tetrahedral and octahedral coordination with oxygen. Aluminum is typically associated with silicon in fourfold coordination and with Fe(III) in sixfold coordination in the same mineral. Often aluminum is coordinated with hydroxyl groups in sixfold coordination and with oxygen in fourfold coordination.

Aluminum coordination with oxygen or hydroxyl is very important in determining the surface charge of minerals. Aluminum hydroxide with sixfold coordination acts as a base, whereas aluminum with fourfold coordination acts as a central atom in an anion. For a given stoichiometry, therefore, the substitution of Al^{3+} for Si^{4+} in a mineral can lead to negative charge deficiency either in interlayers or at edges (Goldschmidt 1954), and can have a great influence on the surface and ion-exchange properties of a mineral.

1.2.1 ALUMINUM IN ROCKS

There are so many minerals containing aluminum that it occurs everywhere in the earth's crust. In igneous rocks, feldspar is the most important aluminum-containing mineral, although feldspathoids, micas, amphiboles, spodumene, and tourmaline, as well as topaz in pegmatites, all contain aluminum. In hydrothermal deposits, zeolite, cryolite, amblygonite, epidote, and chlorite contain aluminum. In metamorphic rocks, feldspar, mica, garnet, cordierite, sillimanite, andalusite, spinel, corundum, kyanite, staurolite, and epidote are the important aluminum-containing minerals. In sedimentary rocks, aluminum-containing clay minerals include kaolinite, illite, smectite, chlorite, and fibrous clays.

Igneous rocks may contain between 0.1 and 21% Al_2O_3. Certain ultrabasic rocks may contain trace amounts of aluminum, whereas nepheline syenites have the highest concentrations of aluminum. Other igneous rocks contain an average of 15% Al_2O_3.

1.2.2 ALUMINUM IN CLAYS

Aluminum is found predominantly in the clay fraction of sedimentary rocks. These clays, which may contain 25-40% Al_2O_3, are derived from the chemical breakdown (weathering) of igneous and metamorphic minerals. During this weathering, cations and silicon are mobilized while aluminum is retained in the clay mineral. The general weathering reaction is:

$$\text{cation-Al-silicate} + H_2O + nH^+ = \text{clay} + \text{cation}^{n^+} \pm H_4SiO_4 \qquad [2\text{-}1]$$

Under extreme weathering, silica is mobilized and the clay mineral is further degraded to aluminum oxide, which forms typical lateritic or bauxitic deposits. Aluminum is concentrated in the leached zone of soils and resembles the development of laterite.

Clay minerals are important in soils and can influence aluminum mobility by dissolution and adsorption processes. Clay minerals are classified into groups based on their structure: "Si-tetrahedral" (T) sheets, "Al-octahedral" (O) sheets, and various substitutions (Van Olphen 1977). These have been classified as two-layer clays (kaolinite group), three-layer clays, four-layer clays (chlorites), and fibrous clays.

The two-layer clays consist of a Si-tetrahedral sheet and an Al-octahedral sheet. They have a constant stoichiometry and a low cation-exchange capacity (CEC), and are nonexpanding. The three-layer clays consist of a sandwich of two Si-tetrahedral sheets on either side of one Al-octahedral sheet. They can be further subdivided into two groups: (i) expanding (smectite, or montmorillonite) group, which has a large CEC and limited substitution of Al for Si in the Si-tetrahedral sheets; and (ii) nonexpanding (illite or degraded mica) group, which has an intermediate CEC and has about 25% of the Si replaced by Al. The four-layer clays are nonexpanding and have a low CEC. Fibrous clays have double chains or are more closely connected by one-dimensional O layers. They are elongated and not well defined.

Clay minerals occur as fine-grained (<1 µm) particles and typically have a high surface area per unit weight. Table 1-1 gives some of their surface characteristics (Van Olphen and Fripiat 1979; Morrill et al. 1982).

The values in Table 1-1 can be considered as typical, although elemental substitutions can change the properties substantially. Montmorillonite tends to be a good cation exchanger because it exchanges

Table 1-1. Surface-related characteristics of some clay minerals (from Van Olphen and Fripiat 1979; Morrill *et al*. 1982)

Characteristic	Kaolinite	Illite	Montmorillonite
CEC (meq·$(100\ g)^{-1}$)	0.1-5	27-37	40-120
Specific surface ($m^2 \cdot g^{-1}$)	10-25	90-112	30-140
Specific CEC ($\mu eq \cdot m^{-2}$)	1.4-2	2.7	7-24
pH - zero point of charge	4.6	6	2.5

on both edges and interlayers, whereas other clays such as illite and kaolinite exchange mostly on the edges. Three generalizations may be made regarding exchangeability (Morrill et al. 1982): exchangeability increases with (i) increasing hydrated radius and decreasing polarizability; (ii) decreasing counterion charge; and (iii) increasing ease of cation hydration.

1.2.2.1 Aluminum Mobilization from Clays

Clay minerals are often classified by soil scientists into "neutral clays" and "acid clays" (Holt and Bruggenwert 1978). The neutral clay is typified by a partially reversible cation-exchange reaction of the sort:

$$M^{m+}\ \text{clay} + mN^{n+} = N\ \text{clay} + nM^{m+} \qquad [2\text{-}2]$$

or

$$M^{m+}\ \text{clay} + mH^{+} = H_{m}\ \text{clay} + M^{m+} \qquad [2\text{-}3]$$

where M^{m+} and N^{n+} are cations.

Acid clays form at low pH values (<5). When the mineral surface becomes saturated with hydrogen ions, there is accelerated inward diffusion of H^{+} and outward diffusion of Al^{3+} resulting in a H^{+}-Al^{3+} surface with the possible exchange:

$$3H^{+} + Al{\equiv}\text{clay} = Al^{3+} + H_{3}^{+}{\equiv}\text{clay} \qquad [2\text{-}4]$$

This is one possible mechanism for aluminum mobilization at low pH.

Alternatively, amorphous $Al(OH)_3$ or gibbsite may exist as surface groups on clays or as individual particles. In such cases the mobility of aluminum is a result of the solubility of the mineral:

$$Al(OH)_{3} + 3H^{+} = Al^{3+} + 3H_{2}O \qquad [2\text{-}5]$$

1.3 FACTORS AFFECTING ALUMINUM SPECIATION AND MOBILITY

Even though aluminum is ubiquitous, its chemistry in natural systems is poorly understood, despite more than 50 years of research by chemists and soil scientists. Results have been ambiguous, because of the multiple interactions between aluminum and both organic and inorganic ligands, the metastability of some of these compounds, and the many kinetic reactions involved. All of this is further complicated by the extreme difficulty of separating particulate and dissolved phases (Wagemann and Brunskill 1975; Danielsson 1982). For example, about half of the aluminum in natural water that passes through a 0.45-µm filter also passes through a 0.1- or 0.02-µm filter. It should be noted, however, that the physical speciation of aluminum in natural waters is highly variable, and the results of a single differential filtration experiment cannot be taken as representative of natural waters in general. The difficulty in separating particulate from dissolved aluminum, although common for many waters, is of particular importance for turbid surface waters, groundwater, and soil extracts.

Aquatic interactions of aluminum involve hydrolysis and complexation with fluoride (F^-), organic compounds, and, to a lesser extent, SO_4^{2-}. Hydrolysis and organic complexation appear to be the more important reactions in natural environments, followed by F^- complexation.

1.3.1 pH

Below pH 4.0 aluminum exists predominantly as a trivalent cation, surrounded by six water molecules: $Al(H_2O)_6^{3+}$ (Manahan 1975). Between pH 4.5 and 6.5, aluminum species include $Al(OH)^{2+}$, $Al(OH)_2^+$, and $Al(OH)_3(s)$. In basic media aluminum exists primarily as the anion $Al(OH)_4^-$.

1.3.1.1 pH and Aluminum Solubility

Aluminum is generally not mobile in near-neutral aqueous solutions but is mobilized in acidic and basic solutions. The amphoteric nature of Al-OH complexes has been known for some time and has been used to explain its geochemical cycling (Stumm and Morgan 1981). The aqueous concentration of aluminum increases at low and high pH primarily because of the hydrolysis of aluminum and its reaction with minerals. Thus, one can approximate the total concentration of aluminum (Al_T) from the solubility product of gibbsite or amorphous aluminum hydroxide in acidic (<pH 5.5) natural waters as follows:

$$10^{+8.0} \text{ or } 10^{+9.7} = \frac{[Al^{3+}]}{[OH^-]^3} \text{ for solubility of } Al(OH)_3 \qquad [2\text{-}6]$$

The first hydrolysis constant for Al^{3+} is:

$$Al^{3+} + H_2O = Al(OH)^{2+} + H^+, \text{ and } 10^{-5} = \frac{[AlOH^{2+}][H^+]}{[Al^{3+}]} \qquad [2\text{-}7]$$

and the ion condition:

$$Al_T = [Al^{3+}] + [AlOH^{2+}] \qquad [2\text{-}8]$$

which results in

$$Al_T = 10^K ([H^+]^3 + 10^{-5}[H^+]^2) \qquad [2\text{-}9]$$

where pK = 9.4 for amorphous aluminum hydroxide and 8 for gibbsite.

Some expected values for the above calculations are:

	Al_T	
pH	$mol \cdot L^{-1}$	$\mu g \cdot L^{-1}$
6.5	$10^{-10} - 10^{-8.6}$	0.003 - 0.17
6.0	$10^{-9} - 10^{-7.6}$	0.03 - 0.8
5.5	$10^{-7.9} - 10^{-6.5}$	0.36 - 0.9
5.0	$10^{-6.7} - 10^{-5.3}$	5.4 - 140
4.5	$10^{-5.4} - 10^{-4.0}$	112 - 2800
4.0	$10^{-4} - 10^{-2.5}$	3000 - 75 000

Measured aluminum concentrations are typically higher than estimated at high pH and lower than estimated at low pH (see Figure 1-1). This is probably the result of problems of filtration as well as slow dissociation kinetics.

1.3.1.2 pH and Aluminum Hydrolysis

Two general approaches that have been used to explain aluminum hydrolysis are (i) formation of reversible mononuclear complexes (Bronsted and Volqvartz 1928; Hartford 1942; Ito and Yui 1953; Schofield and Taylor 1954; Gayer *et al.* 1958; Frink and Peech 1963a; Raupach 1963; Kittrick 1966; Frink and Sawhney 1967; Hem 1968a; Sullivan and Singley 1968; Grunwald and Fong 1969; Nazarenko and Nevskaya 1969; Reesman *et al.* 1969); and (ii) formation of kinetically dependent polynuclear complexes (Brosset 1952; Matijevic and Tezak 1953; Brosset *et al.* 1954; Faucherre 1954; Sillén 1954; Ruff and Tyree 1958; Aveston 1965; Fripiat *et al.* 1965; Hsu 1966; Turner 1968; Smith 1969; Schoen and Roberson 1970; Akitt *et al.* 1972; Chen 1973; MacDonald *et al.* 1973; Patterson and Tyree 1973; Hayden and Rubin 1974; Baes and Mesmer 1976; Nair and Prenzel 1978; Bottero *et al.* 1980).

In most studies, there is strong evidence for the first hydrolysis step: $Al^{3+} + H_2O = AlOH^{2+} + H^+$ with pK 5. However, there is a greater than one order-of-magnitude difference in the pK values obtained experimentally for this reaction alone (Hayden and Rubin 1974; see also Appendix I.0). Table 1-2 compares some values for the first hydrolysis product.

The monomeric hydrolysis model considers only the following species: Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^+$, $Al(OH)_4^-$, and sometimes $Al(OH)_3^0$. The polynuclear models consider a different set of species: Al^{3+}, $AlOH^{2+}$ and $Al_m(OH)_n$, with values of m and n being typically 6,15; 7,17; 8,20; 8,22; 10,24; 13,32; and 14,34, with OH/Al(n/m) ratios of 2.5, 2.4, 2.75, 2.4, 2.5, and 2.4, respectively. As the pH increases from 4.5 to 6.5, aluminum polymerizes and forms gibbsite ($Al_2O_3 \cdot 3H_2O$) or bayerite ($Al(OH)_3$) as an

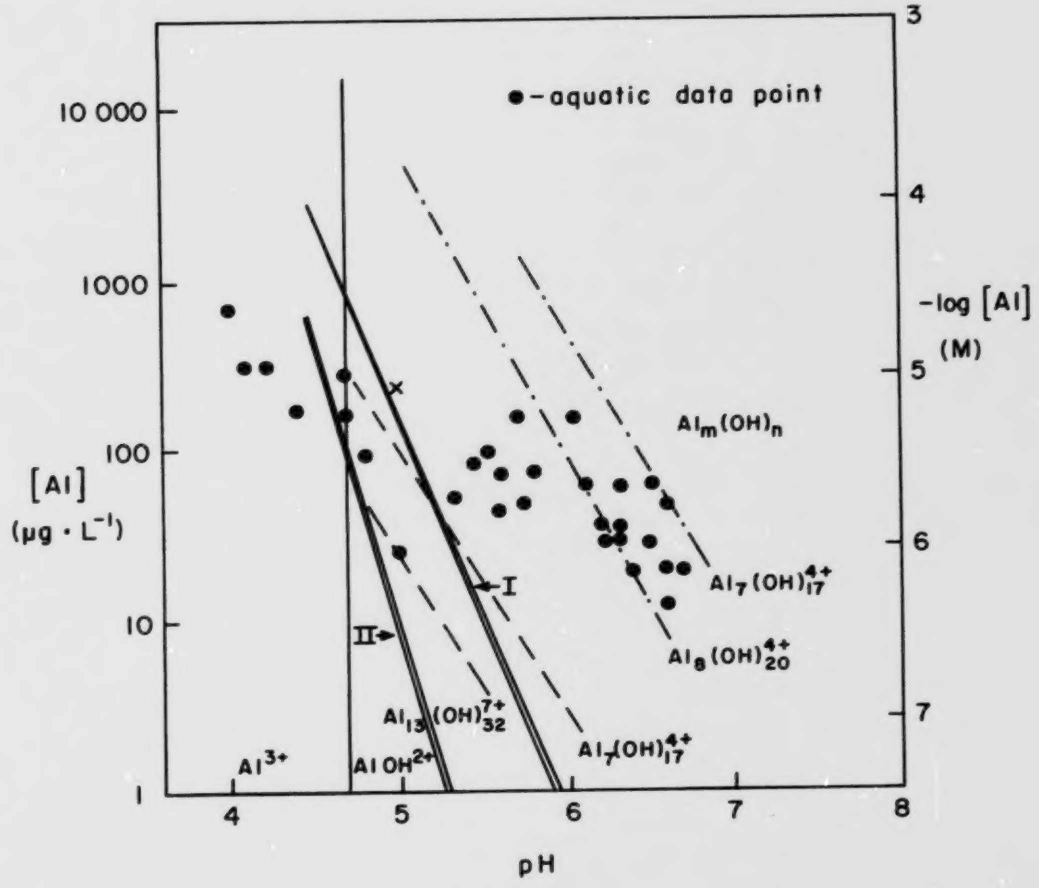


Figure 1-1. Predominance diagram for monomeric (AlOH^{2+}) and polynuclear (Al$_m$(OH)$_n$) species. Aquatic data points reflect lakes from eastern Canada and New England states. The double lines reflect the predicted Al$_T$ for amorphous Al(OH)$_3$ (I) and gibbsite (II) using an Al^{3+} + AlOH^{2+} model. Solid line is for Al^{3+}--AlOH^{2+} equilibria; dashed lines are for Al$_m$(OH)$_n$--AlOH^{2+}--Al^{3+} equilibria.

Table 1-2. Comparison of values of pK, at zero ionic strength, 25°C.

Method	pK_1	Total soluble aluminum (M)	Reference
Potentiometry	4.6	$>10^{-3}$	Hartford (1942)
	4.99		Smith and Martell (1976)
	5.02	10^{-2}-10^{-5}	Frink and Peech (1963a)
	5.03	10^{-3}	Kubota (1956)
Spectrophotometry	5.04	10^{-2}	Nazarenko and Biryuk (1974)

end product (Manahan 1975). The rate of polymerization depends on the concentrations of OH and Al as well as on the ratio of OH to Al. Experiments using a well-defined synthetic solution showed that with a ratio of OH/Al less than 1, only monomers and dimers are present in solution (Hem 1968a). With a OH/Al ratio between 2 and 3, particles approaching 0.1 µm in diameter form within 10 d at 25°C. At a OH/Al ratio in excess of 3, bayerite forms and rapidly precipitates. This indicates that aluminum samples can 'age' with time, resulting in changes in size, speciation, and solubility.

Most potentiometric studies in dilute solutions ($<10^{-4}$ M Al) show good evidence for the presence of monomeric Al^{3+} - $AlOH^{2+}$ but not for intermediate monomeric complexes.

Figure 1-1 indicates the predominant monomeric and polynuclear species. Superimposed on this diagram is the range of concentrations of total aluminum for some natural samples. A more complete summary for other hydrolysis species is found in Appendix I.0. It is apparent that the field of predominance of mononuclear aluminum species is very small. At the same time, the ambiguities in the pH range of 5 to 7 are emphasized by the large difference in values obtained for $Al_7(OH)_{17}$ by two different studies (e.g. lines I and II, Figure 1-1).

From the diagram one is tempted to conclude that a workable model contains Al^{3+}, $AlOH^{2+}$, $Al(OH)_4^-$, and $Al_{13}(OH)_{32}^{7+}$. Furthermore, the polynuclear complex is geometrically a multiple of the basic gibbsite unit. Others (Matijevic *et al.* 1961; Hayden and Rubin 1974) have suggested better evidence for the $Al_8(OH)_{20}^{4+}$, although Hsu (1977) eliminated this species because of the implied repulsions of Al^{3+}.

1.3.1.3 Kinetics of Reaction

When the ratio of OH to Al is greater than 1, aluminum hydrolysis is very slow. It may take several months to reach equilibrium (Hayden and Rubin 1974). Some studies have been carried out at high temperature to accelerate this reaction. In other studies (de Hek *et al.* 1978) careful experimental procedures were developed to eliminate metastable phase formation, because of short-term excess concentration of base during titration. Because formation of metastable polynuclear complexes becomes more probable with increasing OH/Al, many experimental results may be operationally defined and are, therefore, valid only under certain conditions. This contributes to the wide range in results.

Turner (1969, 1971, 1976) and Turner and Sularman (1971) studied the kinetics of hydrolysis of mononuclear and polynuclear complexes in the laboratory using an extraction procedure after complexing aluminum with oxine. They found that the hydrolysis of mononuclear complexes is virtually complete within some tens of seconds, whereas polynuclear species react very slowly. The release of aluminum from a freshly precipitated phase (i.e., reversible reaction) has also been demonstrated.

1.3.2 ORGANIC MATTER

Another factor affecting aluminum mobility is organic matter found in soils. Aluminum can coagulate the common cations and is readily adsorbed to organic substances (Morrill et al. 1982). The mobility of aluminum, therefore, can be significantly altered by organic compounds.

There are only a few well-defined data available for model aluminum-organic complexes. These are given in Appendix II.0. Table 1-3 is a summary for organic complexes of pK_a values along with $p\beta_i$ as defined for:

$$HA = H^+ + A^- \text{ (dissociation of a weak acid, HA)} \qquad [2\text{-}10]$$

$$K_a = \frac{[H^+]\,[A^-]}{[HA]} \text{ etc.; } pK_a = -\log\,(K_a) \qquad [2\text{-}11]$$

and for $M + iL = ML_i$ (complexation of metal M with ligand L)

$$\beta_i = \frac{[ML_i]}{[M]\,[L]^i}\ ;\ p\beta_i = -\log\,(\beta_i) \qquad [2\text{-}12]$$

The general impression is that simpler acids form weaker complexes with aluminum, whereas aromatics form stronger complexes. There are exceptions, such as 4-hydroxybenzoic acid, which appear to depend upon substituted groups. The value of these stability constants is questionable, as they were determined at low pH (1.65-3.5). In addition, a pβ of 4 has been estimated for the aluminum-fulvic complex; however, no further details were given (Schnitzer 1971).

It may be possible to extend our understanding of complex formation of aluminum with organics by comparison with other ions. A comparison of stability constant values for Fe^{3+} complexes and Al^{3+} complexes is shown in Figure 1-2 for inorganic and organic complexes. The correspondence is quite good. If the Fe^{3+} complex is known, a provisional value can be estimated using this correlation.

1.3.3 FLUORIDE

Fluoride forms complexes of the form AlF_x, where the value x varies from 1 to 6. AlF_x complexes predominate in slightly acidic water, whereas $Al(OH)_x$ complexes predominate in alkaline water (Hem 1968a). Fluoride levels in uncontaminated natural waters range from approximately 0.01 to 0.1 $mg \cdot L^{-1}$. For these concentrations of fluoride, AlF^{2+} and AlF_2^+ would be predominant complexes. Fluoride also forms complexes with the other cations and organics, and about 15% is bound at pH 4. Other

Table 1-3. Comparison between the dissociation constants and the complex formation constants of aluminum with some organic acids.

Acid	pK_{a_1}	pK_{a_2}	pK_{a_3}	log β_1	log β_2	log β_3
Formic	3.75			1.36		
Acetic	4.76			1.50		
Propanoic	4.87			1.69		
Butanoic	4.82			1.58		
Benzoic	4.21			12.09$^{\alpha}$		
Nitroacetic	1.68			0.48		
Oxalic	1.27	4.27		6.06	11.09	15.12
Oxidiacetic	2.97	4.37		3.16	5.25	
Thiodiacetic	3.24	4.56		1.93	12.34$^{\beta}$	
D-tartaric	3.04	4.37		5.32	9.77	
Meso-tartaric	3.04	4.37		5.62	9.95	
Salicylic	2.97	13.59		12.9	23.2	29.8
Phthalic	2.95	5.42		3.18	6.32	
5-Sulfosalicylic	2.33	11.32		12.3	22.0	27.8
Catechol	9.45	12.8		16.9	30.5	39.4
Citric	3.13	4.76	6.40	7.37	13.9	
4-Hydroxybenzoic	4.57	9.46		1.66		
Malic	3.46	5.10		5.14	8.52	
Catechol-5-sulfuric	8.50	12.8		16.6	29.9	39.2
Tiron	7.66	12.6		16.7	30.3	40.0
Chromotropic	5.33	15.6		17.1	29.8	

Note: Data are given for zero ionic strength. The second set of acid dissociation constants are those used in the specific aluminum complex determination. See Appendix II.0 for details and references.

$^{\alpha}$ $Al^{3+} + B^{-} + OH^{-} = Al\ OH\ B^{+}$.

$^{\beta}$ $Al^{3+} + OH^{-} + TDA^{2-} = Al\ OH\ TDA$ (TDA = thiodiacetic acid).

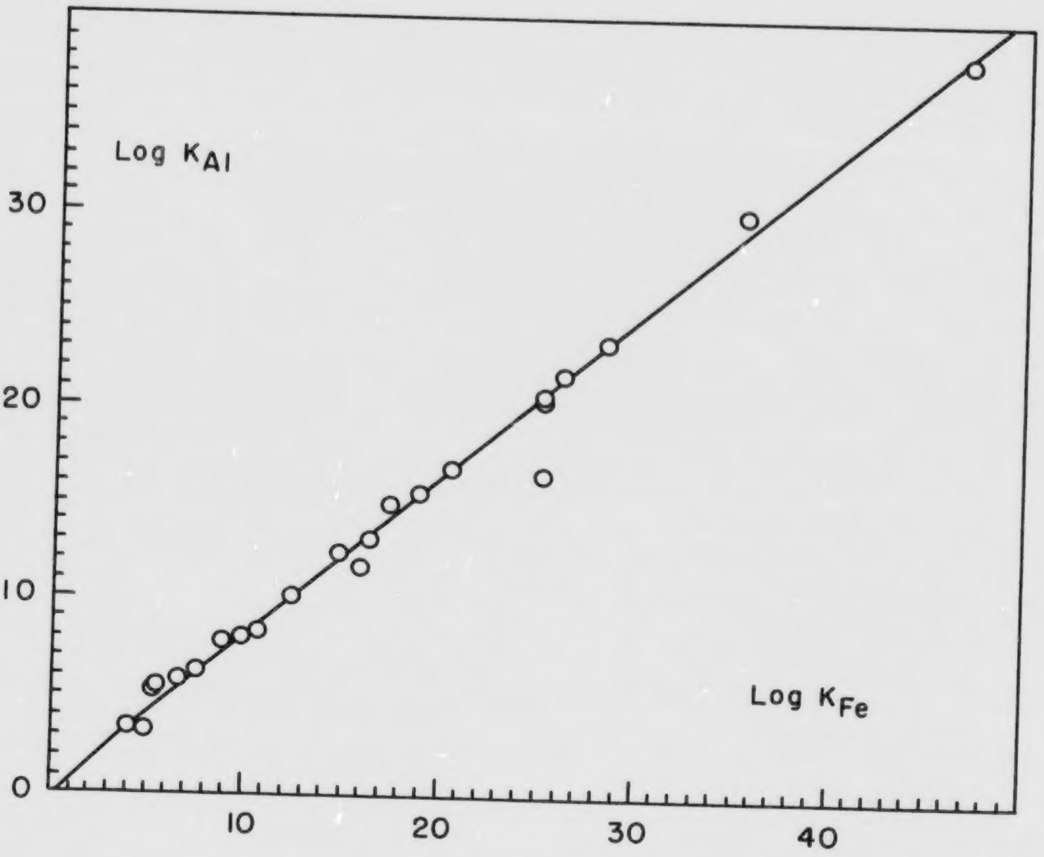


Figure 1-2. Plot of stability constants of Al^{3+} and corresponding Fe^{3+} complexes. Linear regression equation:

$\log K_{Al} = 0.828 \log K_{Fe} - 0.325$
$r = 0.985, \quad n = 23$
Error of estimate for $\log K_{Al} = \pm 1.14$
Error of slope = ± 0.022
Error of intercept = ± 0.449

Complexes and data are from Kramer (1981); see also Table I-1 in Appendix I.0.

laboratory studies have suggested more complex aluminum hydrolysis products involving SO_4^{2-} and F^- (Matijevic et al. 1961) as well as monosilicic acid (Luciuk and Huang 1974) and phosphate (Ng Kee Kwong and Huang 1978).

1.3.4 SULFATE

The two major complexes involving SO_4^{2-} include $Al(SO_4)^+$ and $Al(SO_4)_2^-$ (Hem 1968b). The calculation of the aluminum distribution among the major aluminum complexes as a function of F^-, SO_4^{2-}, and OH^- concentrations is illustrated in Figures 1-3, 1-4, and 1-5. These figures indicate that $Al(SO_4)_x$ is present in appreciable concentrations only at low pH and high SO_4^{2-} concentrations, conditions which are seldom encountered in natural water.

1.4 ADSORPTION REACTIONS INVOLVING ALUMINUM

1.4.1 CLAYS

The acidity of clay soils is thought to be the result of H^+-Al^{3+} interaction. Aluminum adsorbed on soils or clays may be exchanged by H^+ and other cations, held strongly ("fixed"), or precipitated on the surface as $Al(OH)_3$ or as some other more complex substance. Recently the adsorption of sulfate on aluminum oxides or iron oxides has been postulated to be an important factor in acid/base exchange (Johnson and Cole 1977; Johnson and Henderson 1979).

In the mobilization or fixation of aluminum on any membrane, the importance of other cations, especially Ca^{2+} and H^+, must be considered. This is true for clays (Wiklander 1980), tree rootlets (Hüttermann 1984), and fish gill membranes (Howells et al. 1983).

The nature of aluminum exchanged from clays has been documented only for montmorillonite and illite. Polynuclear hydroxypolymers adsorb on illite and follow a Langmuir isotherm (Columbera et al. 1971). The proposed mechanism is hydrogen bonding between the OH groups of the polymer and silica groups on the illite. Aluminum can be exchanged on montmorillonite for a OH/Al ratio ranging from 0 to 2.5, with polynuclear complexes being exchanged more readily. It appears that only Al^{3+} is exchanged from vermiculite (Veith 1977).

Dissolution/desorption experiments were carried out to determine the form of the mobile aluminum. Using stoichiometric relationships, Ragland and Coleman (1960) suggested that the acid-leachable solid form of aluminum is $Al(OH)_3$, but other studies (Frink and Peech 1963b) have reached different conclusions. In addition, there may be incongruent adsorption/desorption of aluminum. For example, Veith and Sposito (1979) showed that a sodium sulfonic resin adsorbs aluminum with a higher OH/Al ratio than is present in solution.

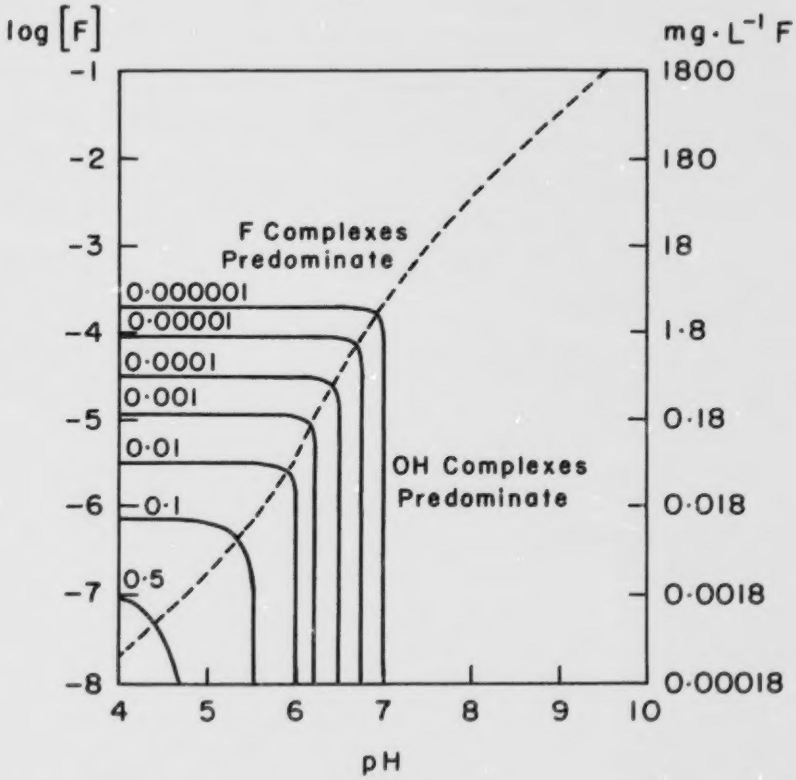


Figure 1-3. Predominate form of aluminum complex and ratio of free aluminum activity to total dissolved aluminum as a function of pH and fluoride activity (from Hem 1968b).

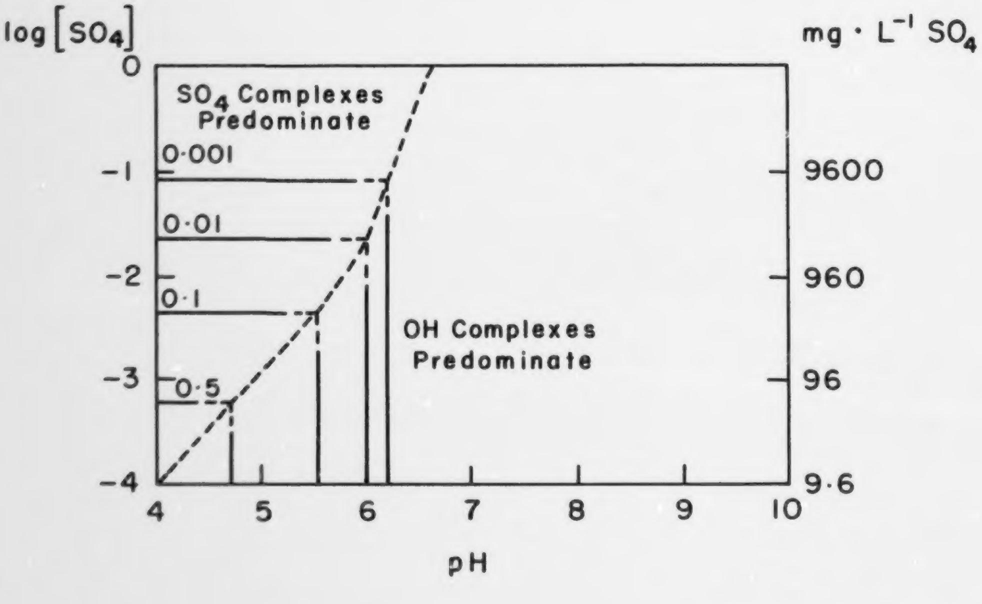


Figure 1-4. Predominate form of aluminum complex and ratio of free aluminum activity to total dissolved aluminum as a function of pH and sulfate activity (from Hem 1968b).

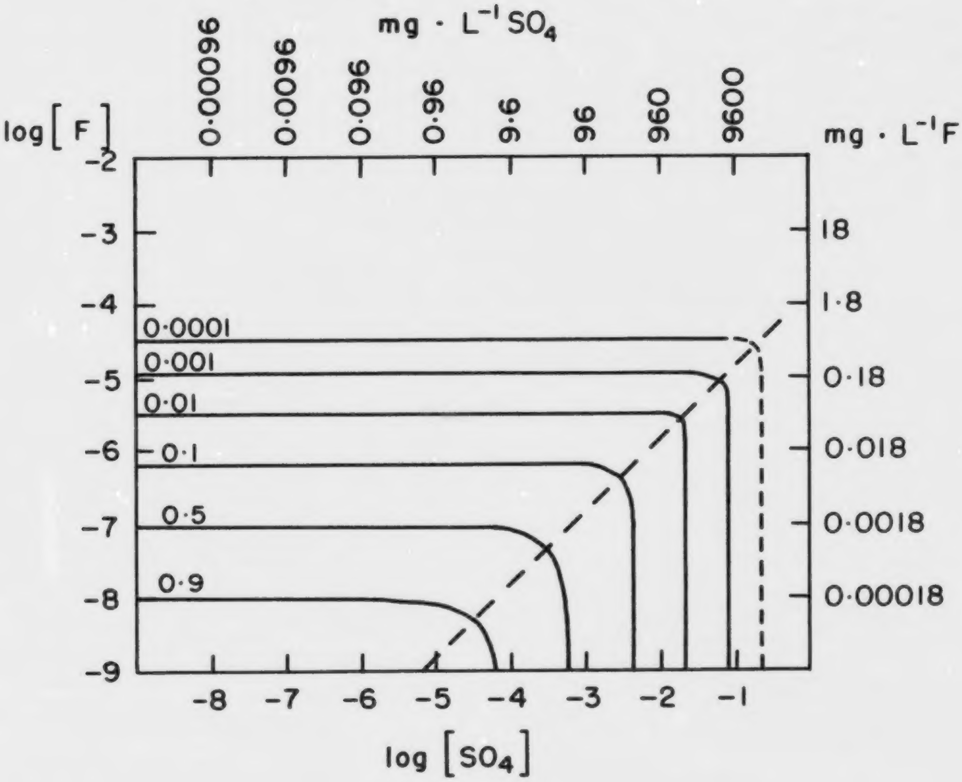


Figure 1-5. Predominate form of aluminum complex and ratio of free aluminum activity to total dissolved aluminum as a function of sulfate and fluoride activity at low pH (from Hem 1968b).

In summary, monomeric and polynuclear forms of aluminum are adsorbed, with OH/Al and other cations being the important variables controlling the exchange. Nonexchangeable aluminum was originally assumed to be precipitated on a surface as $Al(OH)_3$, although more recent studies (Hsu and Rich 1960; Hsu and Bates 1964a; Brown and Newman 1973; Veith 1977; Veith and Sposito 1979) propose $AlOH^{2+}$ ($OH/Al < 2.5$) to be the adsorbed species. When calcium- or sodium-saturated exchanges are studied, a polymer model, possibly with a hexamer ring, has been invoked (Hsu and Bates 1964a).

Information on forms of aluminum fixed on kaolinite and organic matter is lacking.

1.4.2 PHOSPHATE

Aluminum has the ability to precipitate dissolved PO_4^{3-}. Alum is added in sewage treatment plants precisely for this reason. Adsorption of orthophosphate on hydrous Al_2O_3 appears to be a function of pH and the total PO_4^{3-} concentration (Huang 1975). At 10^{-4} M PO_4^{3-}, maximum adsorption occurs at pH 4.5. At lower concentrations of PO_4^{3-}, maximum adsorption occurs over a broader pH range.

1.4.3 SULFATE SORPTION AND MINERAL FORMATION

Podsol-, spodosol-, and ultisol-type soils have been shown to adsorb SO_4^{2-} ions. This "adsorption" seems to be associated with iron and aluminum oxyhydroxide fractions in the upper leached zone of the soil (Johnson and Cole 1977; Johnson and Henderson 1979; Christophersen and Wright 1981), and has been modelled as a simple linear adsorption/desorption reaction (Christophersen et al. 1982; Electric Power Research Institute 1983). Using this model, the same equivalents of SO_4^{2-} and H^+ are adsorbed in order to maintain electroneutrality. An acid pulse occurs when the SO_4^{2-} is desorbed because H^+ is also desorbed. Hence, buildup and release of SO_4^{2-} produce changes in acid concentrations.

Specific Al-SO_4 minerals have also been discussed in relation to uptake of aluminum and sulfate by soil. The stability of Al-SO_4 minerals has been compared with that of gibbsite and kaolinite (Nordstrom 1982). Alunite ($Al_2(SO_4)_3 \cdot 17H_2O$) appears to be stable in the pH 4-7 range for many waters. Solubility calculations for alunite and basalunite fit analytical results for the lower B soil horizon and upper leached zone, respectively, in a Swedish forest (Nilsson and Bergkvist 1983).

Jarosites ($MR_2(SO_4)_2(OH)_6$; where $M = Na^+$, K^+, NH_4^+, or H^+, and $R = Fe^{3+}$ or Al^{3+}) were shown to form slowly in the laboratory by degradation of common aluminosilicate minerals (Ivarson et al. 1982). Furthermore these minerals were also found in various acidic organic soils in Canada (Ross et al. 1982), possibly resulting from microbial alteration of sulfur.

There is a difference in the number of variables required to define the system, depending upon the model used. The simple sulfate adsorption/desorption model requires only the sulfate concentration. The aluminosulfate model requires pH, total aluminum, and sulfate ion concentrations, as well as a knowledge of the ion complexes. The "jarosite" model requires concentrations of K^+, Na^+, Li^+, NH_4^+, and Fe^{3+}, as well as the mineral stoichiometry. If the minerals dissolve congruently there will be a range in acid release, depending upon the mineral stoichiometry.

1.5 CONCENTRATIONS AND AVAILABILITY IN VARIOUS ENVIRONMENTS

1.5.1 SURFACE WATERS, GROUNDWATERS, AND SOIL SOLUTIONS

One must carefully scrutinize data for aluminum in natural waters. Many of the analyses give data for unfiltered samples (total aluminum) only. Even values determined using samples filtered through 0.45-µm media may contain substantial contributions from colloidal aluminum. This is perhaps best illustrated by the fact that filtered turbid waters or groundwaters have higher aluminum concentrations than do lakes at the same pH. Part of the increase in aluminum is explained by the high aluminum content of very fine suspended particulates.

The problem of separation of particulate and dissolved phases by filtration is generally avoided in dystrophic waters by filtration through 0.45-µm media. However, an added complication is that major portions of aluminum may be associated with dissolved organic material (see Section 1.3.2).

Most water pollution problems involving aluminum are associated with acidification. For example, in coal strip mining (Campbell and Lind 1969) the resulting decrease in pH of the water increased the aluminum concentration with resultant effects on biota (Collier et al. 1964). However, after mining and acidification were stopped, the aluminum concentration decreased rapidly (Curtis 1972). This reflects the rapid adsorption of aluminum on particle substrates.

Aluminum in the soil solution also increases with decreasing pH. However, aluminum is fixed by organic matter and is adsorbed to a greater degree in soil solution than in lake or river water, simply because of the larger soil particle surfaces available for adsorbing aluminum.

Proposed tolerable aluminum concentrations in agricultural irrigation waters are 1 $mg \cdot L^{-1}$ for long-term use and 20 $mg \cdot L^{-1}$ for short-term use (Sorenson et al. 1974). It is not clear whether these values are for total or filtered aluminum; if total, the values would be meaningless. In addition, other important factors, such as pH, hardness, and dissolved organic carbon, were not considered.

Similarly, the maximum acceptable concentration for aluminum in drinking water for livestock was 5 mg$\cdot$L^{-1} (Sorenson et al. 1974). Interestingly, there appears to be no specified limit for aluminum in municipal drinking water supplies.

Aluminum concentrations in water correlate with the characteristics of the rocks and soils with which the water comes into contact. Rocks and soils (via their buffering capacities) act as surrogates for solution pH, which is the most important factor controlling aluminum concentrations. Granite or other acidic igneous and metamorphic rocks, and tills or the sediments derived from them, may be associated with surface water aluminum concentrations in excess of 10 µg$\cdot$L^{-1}; associated groundwaters may have levels 2 to 10 times higher. Unmetamorphosed basic igneous and metamorphic rocks and associated sediments may have aluminum concentrations near 1 µg$\cdot$L^{-1}, whereas calcareous sediments may have aluminum concentrations below 0.1 µg$\cdot$L^{-1}. Aluminum concentrations may be negligible in waters from sediment and rocks that have more than 5% (by weight) of clay-sized particulates, because of pH buffering and adsorption.

1.6 METHODS FOR AQUATIC SPECIATION OF ALUMINUM

Although a great deal remains to be understood about aquatic chemistry and speciation of aluminum, there appears to be some agreement on general categories of aluminum species that can be defined in an operational/analytical sense:

I) Total dissolved aluminum
II) Mononuclear aluminum
III) Polynuclear aluminum
IV) Organic aluminum

As previously noted, about one-half of the total dissolved aluminum (Category I) will pass through a 0.45-µm filter and will be retained on a 0.02- to 0.1-µm filter. (Again, it should be noted that the results of a single differential filtration experiment cannot be taken as representative of natural waters in general.) This particle size effect appears to be more important in clear waters than in organically colored waters, perhaps because of the effect of large organic macromolecules and the influence of the particles on the pore size of the filter paper. There may also be an influence of adsorption of small aluminum particles on organic substrates. If this is true, it is not known what portion of immediately reactive aluminum (Category II - generally considered to include biologically active and potentially toxic forms of aluminum) would adsorb on the organic substrates if they were concentrated on the filter medium. It is also not known whether the aluminum retained on the filter medium is biologically active. In short, it is not clear whether samples should be filtered to obtain representative values, and, if they are filtered, what size filter should be used. Mononuclear aluminum (Category

II) is generally assumed to consist of the simple inorganic (OH^-, F^-, and SO_4^{2-}) complexes and perhaps simple low-molecular-weight organic complexes of aluminum. This category is generally characterized by rapid reaction with a chromophoric complex (oxine, ferron, catechol), fluorescence medium (Lumogallion), or an exchange medium such as Chelex. One analytical approach is to define a specific time for the reaction, after which the complex is extracted and measured; another approach is to follow the kinetics of the reaction and to apply a simple (first-order) model to obtain the "fast-reactive" aluminum.

Polynuclear aluminum (Category III) is generally obtained by difference. In some cases this might involve the difference between the measured total soluble and the mononuclear aluminum, and would therefore include the organic and inorganic fractions. Alternatively, a sample may be digested at elevated temperature with a chromophoric or fluorescent complex so that polynuclear complexes will react with mononuclear complexes. The difference between a digested and nondigested sample would then be designated as polynuclear aluminum.

Organically complexed aluminum (Category IV) is generally obtained by size exclusion, photolytic oxidation, or an exchange column. In the first case, dialysis membranes (molecular weight cutoff approximately 10^3 daltons) are used to exclude the organic fraction. This would probably not exclude simple organic complexes if they exist. In the photolytic oxidation method, a solution of hydrogen peroxide maintained at a constant pH is used in conjunction with a strong UV source to decompose all of the organic matter. The increase in the amount of aluminum available for reaction (i.e., Category II) is then considered to be the organically bound aluminum. In the ion-exchange technique, inorganic forms of aluminum are presumed to be retained on a cation-exchange column, whereas high-molecular-weight and/or very stable organically bound forms are presumed to pass through the column. The difference in analysis for total aluminum before and after column treatment is reported as organically bound aluminum.

Any and all of the concepts behind any given method or combination of methods for aluminum speciation can be criticized. Hence all schemes for analysis must be considered operationally defined. For example, it is not clear in the dialysis method what directly or indirectly may influence aluminum diffusion. Techniques for determining rapidly reactive (mononuclear) aluminum are arbitrary and presume that polynuclear species do not react in a similar manner. This has not been rigorously demonstrated. Similarly, in the case of the rapid-reaction (15-s) techniques, it is not clear that all monomeric species react with the complex in question. Furthermore, most techniques require pH adjustment which can, and probably does, change the hydrolysis forms. If there are fine aluminum substrates present in the sample then even more difficulties can arise. This is most important if an exchange column is used, because the nature of the sample will be modified dramatically when passing through the column.

There have been many schemes developed and used quite extensively to determine the apparent speciation of aluminum in natural waters. Most of the protocols focus on Category II, monomeric aluminum. Driscoll (1980) developed a method using ferron for determining rapidly reacting aluminum. An improvement was to use oxine rather than ferron in order to avoid interferences from other substances (Playle et al. 1982). Organics were separated using a cation-exchange column, and total aluminum was determined by flameless atomic absorption (FAA) spectroscopy.

LaZerte (1984) determined monomeric aluminum by reaction with oxine at pH 8.1 within a period of 15 s. He also separated organic aluminum by 24-h dialysis using a membrane with a cutoff molecular weight of 10^3 daltons.

Campbell et al. (1983) determined the reactive (monomeric) aluminum in a more traditional manner by equilibration with Chelex resin. This was followed by use of peroxide and UV photolysis to determine the organically bound aluminum. In more recent studies (see Appendix III.0), however, they found that the polynuclear aluminum species described by Turner (1976) reacted completely with Chelex. Thus, with simple systems, a good time separation was found between reactions of fulvic acid and inorganic complexes of aluminum; however, in samples of natural water, an intermediate reaction was observed with two apparent rates of reaction reflecting "fast" and "slow" reactive aluminum.

The use of the fluoride electrode was also suggested for aluminum speciation. In this technique, the electrode is presumed to measure the free ionic form. The difference between a total fluoride measurement and the free fluoride gives the bound fluoride which is presumed to be complexed with aluminum. Other soluble monomeric species can then be calculated.

Kramer et al. (1981) used a kinetic analytical approach for speciation involving the fluorimetric measurement of aluminum-Lumogallion. Using simple first-order kinetics, they separated the data into "fast" and "slow" reactive aluminum.

An attempt has been made to compare the different speciation methods (LaZerte and Playle 1984). The "free" fluoride/total fluoride method agreed with results from the "fast" reactive aluminum of the kinetic Lumogallion method. Total aluminum determined by digestion and Lumogallion fluorescence compared well with flameless atomic absorption analysis, except for high organic waters where the Lumogallion technique tends to underestimate total aluminum probably because of the nonreactivity of aluminum-organic complexes. The column ion-exchange method gives results about 20% higher than the dialysis/oxine method. The Chelex exchange method appears more robust and apparently separates all but high- molecular-weight organics from total aluminum.

Figures 1-6 through 1-8 show schematics of the speciation techniques discussed above.

There are other chromophores that form strong complexes with aluminum, and these can be used instead of ferron and oxine. Catechol violet, for example, was used by Helliwell et al. (1983) to define "monomeric" aluminum (Category II). Also, Lumogallion (a fluorescing aluminum complex) can be used in a similar manner (Hydes and Liss 1976) to define "monomeric" aluminum.

1.7 ALUMINUM HYDROXY COMPLEXES

Aluminum forms mononuclear and polynuclear hydroxy complexes over a wide pH range; however, most aluminum-ligand studies have been carried out at low pH in order to avoid the problem of aluminum hydrolysis. One must then question the relevance of literature data on aluminum complexes for many natural systems. Öhman and co-workers have recently studied reactions of Al-OH with a number of organic ligands (citrate - Öhman and Sjöberg 1983a; gallate - Öhman and Sjöberg 1981, 1982; 1,2-naphthoquinone-4-sulfonate/1,2-dihydroxy-naphthalene-4-sulfonate - Öhman et al. 1983; pyrocatecholate - Öhman and Sjöberg 1983b; salicylate - Öhman and Sjöberg 1983c) and carbonic acid (Öhman and Forsling 1981) over wide ranges of pH and metal and ligand concentrations. The experimental technique is to carry out EMF titrations and to minimize the difference between the titration curves and the perceived ligand model. Thus experimental results are obtained over concentration ranges similar to natural systems and without preconceived conditions or assumptions regarding complexes other than limitations placed by stoichiometric considerations and components. It is to be expected that results from this type of aluminum complexation study will replace the more simplistic results now being used and will add complexity as well as sophistication to aqueous aluminum chemistry.

It would be most instructional to carry out,, in parallel, the operationally defined extraction studies (e.g., Figures 1-6, 1-7, and 1-8) on the above systems in order to better assess the nature of the complex being separated. This is probably most important for any technique using ion exchange because it is highly probable that aluminum complexes will dissociate within the ion-exchange column. Because some of the complexes may react at different rates, the time of contact with exchangers or competing ligands must be carefully controlled.

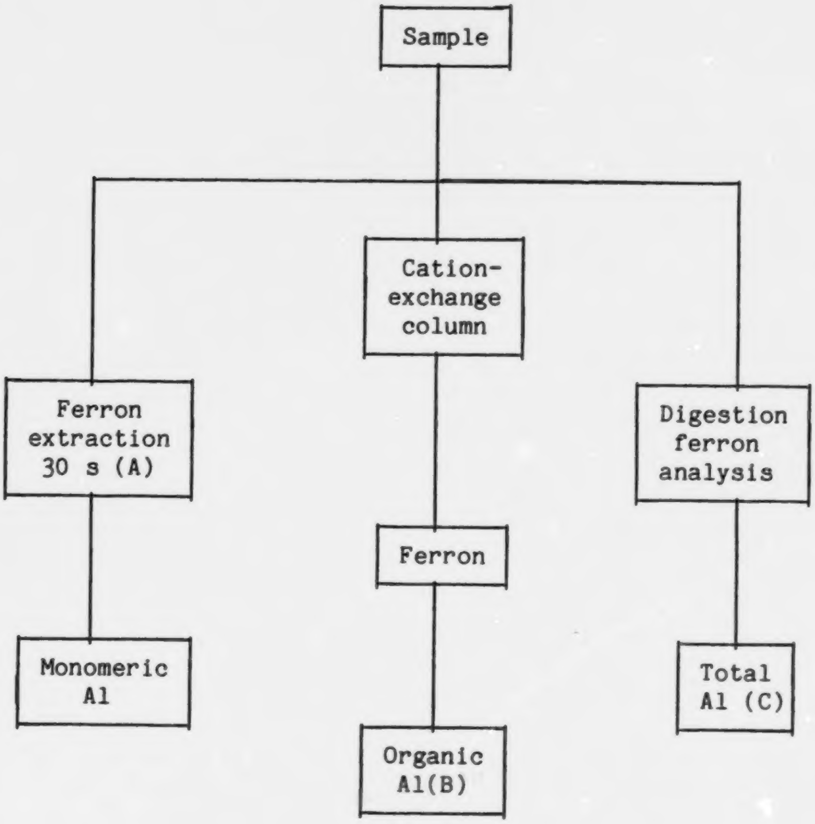

Sample
Cation-exchange column
Ferron extraction 30 s (A)
Digestion ferron analysis
Ferron
Monomeric Al
Total Al (C)
Organic Al(B)

Figure 1-6. Schematic for aluminum speciation using Driscoll (1980) method. C - A = polynuclear aluminum.

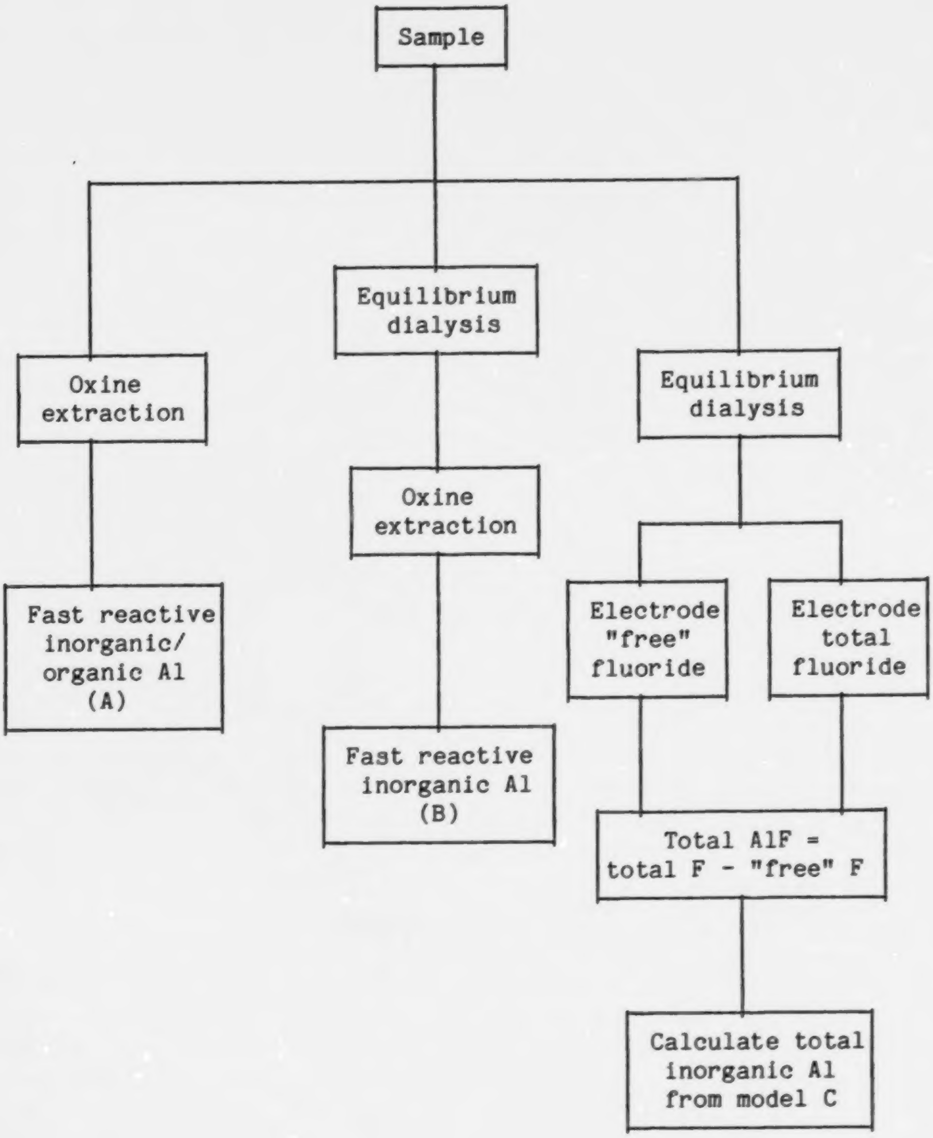
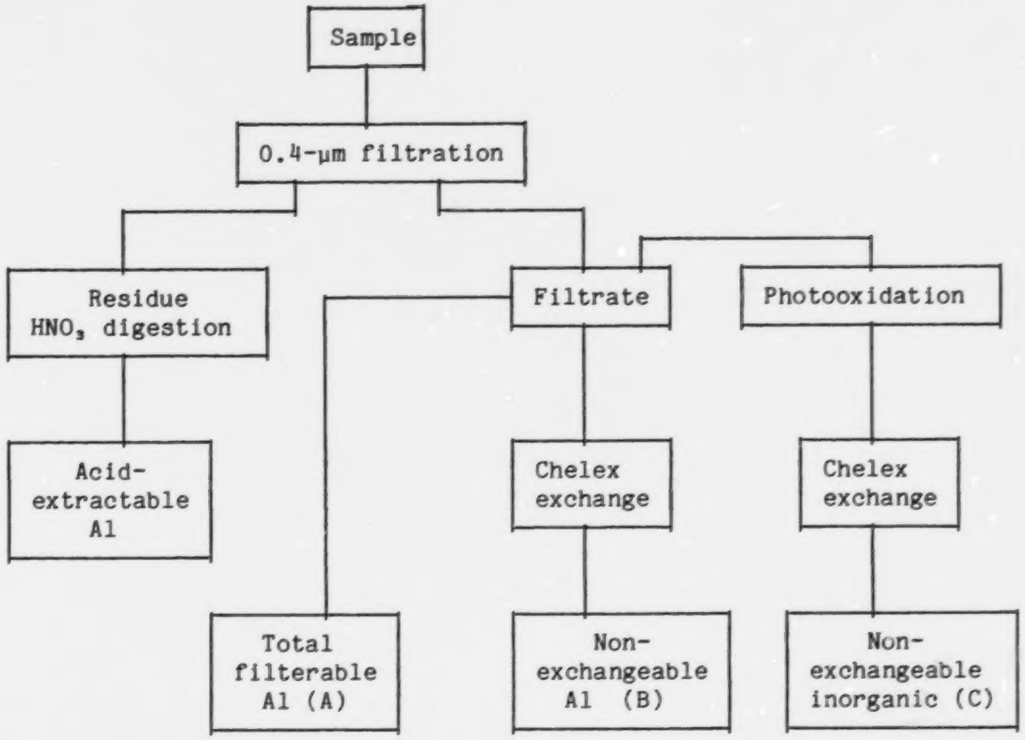

Sample
Equilibrium dialysis
Oxine extraction
Equilibrium dialysis
Oxine extraction
Fast reactive inorganic/ organic Al (A)
Electrode "free" fluoride
Electrode total fluoride
Fast reactive inorganic Al (B)
Total AlF = total F - "free" F
Calculate total inorganic Al from model C

Figure 1-7. Schematic for aluminum speciation using LaZerte (1984) technique. Analyses for aluminum are done by GFAA after oxine extraction in MIBK. Compare C with B.


Sample
0.4-µm filtration
Residue HNO₃ digestion
Filtrate
Photooxidation
Acid-extractable Al
Chelex exchange
Chelex exchange
Total filterable Al (A)
Non-exchangeable Al (B)
Non-exchangeable inorganic (C)

A - B = Exchangeable filterable organic and inorganic Al

B - C = Nonexchangeable filterable organic Al

Figure 1-8. Schematic for aluminum speciation using Campbell et al. (1983) method. Aluminum analyses were performed by furnace atomic absorption.

2.0 ALUMINUM CHEMISTRY OF INLAND WATERS

Magda Havas

Institute for Environmental Studies
University of Toronto
Toronto, Ontario M5S 1A4

2.1 INTRODUCTION

Historically, there has been little concern about aluminum in the aquatic environment because concentrations were thought to be low and not particularly harmful to aquatic biota. Recently, however, elevated concentrations of aluminum in fresh water have been found in regions exposed to acidic precipitation, which leaches aluminum from the terrestrial watersheds into the aquatic environment (Braekke 1976; Cronan and Schofield 1979; Hultberg and Wenblad 1980; Dickson 1980). Studies indicate that relatively low concentrations of aluminum (less than 0.2 $mg \cdot L^{-1}$) can be harmful to aquatic organisms (Fivelstad and Leivestad 1984; Skogheim and Rosseland 1984; Clark and LaZerte 1985; Hutchinson and Holtze 1985; Kramer and Hummel 1985). The losses of some fish populations in North America (Schofield and Trojnar 1980) and in Scandinavia (Muniz and Leivestad 1980a) have been attributed, in part, to elevated concentrations of aluminum in the water column.

In fresh water, the chemistry of aluminum can be quite complex. Recent studies have demonstrated that aluminum can exist as a free ion (Al^{3+}); it can be bound to both organic and inorganic ligands; or it can be absorbed by solid particles. Because the toxicity of aluminum is strongly influenced by its chemical form and because many of the earlier studies failed to consider the complex chemistry of aluminum, these studies must be interpreted with caution. The purpose of this and the following chapter is to summarize the information available on the fate and transport, concentrations, and chemical forms of aluminum in the aquatic environment (Chapter 2) and to assess the effects of aluminum on aquatic biota (Chapter 3). Please refer to Chapter 1 for a more detailed examination of aluminum geochemistry.

2.2 SOURCES OF ALUMINUM

Most of the aluminum in fresh water is derived from contact with soils, sediments, and, to a lesser degree, bedrock, which generally have aluminum levels between 1 and 8% (Bowen 1979). Atmospheric precipitation is another source of aluminum in fresh water (Table 2-1). Aluminum concentrations in precipitation are generally low (less than 0.02 $mg \cdot L^{-1}$), although they can be greater than 0.2 $mg \cdot L^{-1}$ (Sorenson _et_ _al_. 1974; Bowen

Table 2-1. Concentration of aluminum in precipitation and in suspended particulates.

Location		Comments	Al concentration ($\mu g\cdot L^{-1}$)	Reference
Canada	S.E., rural	Atmosphere	0.04-0.39$^{\alpha}$	Sorenson *et al.* 1974
		Rain	520-1120	
		Snow	70-1300	
U.S.A.	East Chicago	In suspended particulates	2.18$^{\alpha}$	Dams *et al.* 1970
	Niles, Michigan		1.2$^{\alpha}$	Zoller and Gordon 1970
	Cambridge, Mass.		0.15-2.5$^{\alpha}$	(cited by Woolrich 1973)
U.S.A.	N.E. Minnesota	Snow cores		Eisenreich *et al.* 1980
	Agricultural (west)	pH 5.32	249	
	Forest Transition	pH 5.00	103	
	Forest (east)	pH 4.64	56	
U.S.A.	Hubbard Brook, N.H.	Precipitation	18	Eaton 1983
Norway			≤20	Gjessing *et al.* 1976
Norway	Birkenes	pH 4.24 precipitation (Nov. 1972 to Oct. 1978)	<54	Christophersen and Wright 1980
Netherlands		During continental periods	92	Asman and Slanina 1980
		During maritime periods	40	
Czechoslovakia	Rural area 40% forest cover	Precipitation (Sept. 1977 to Aug. 1978)	60	Molan 1980
Canada	N.W., 1971	Clean air	0.066$^{\alpha}$	Bowen 1979
Norway	Northern, 1974	"	0.032$^{\alpha}$	
Shetland	1976	"	0.060$^{\alpha}$	
South Pole		"	0.00082$^{\alpha}$	
Europe	Median (range)	Contaminated air	0.6$^{\alpha}$ (0.16-2.9)$^{\alpha}$	Bowen 1979
North America	"	"	2.0$^{\alpha}$ (0.15-3.5)$^{\alpha}$	
Japan	Range	"	- (1.6-6.2)$^{\alpha}$	
Etna Volcano		"	20$^{\alpha}$	
Milan		Atmospheric dust	17 000$^{\beta}$	Bowen 1979
London		"	54-8000$^{\beta}$	
Ocean		"	8000-105 000$^{\beta}$	
N. Hemisphere		Oceanic air	0.121	Bowen 1979
S. Hemisphere		"	0.012	
Average value			0.15-3.5$^{\alpha}$	Bowen 1979

$^{\alpha}$ Units are $\mu g\cdot m^{-3}$.

$^{\beta}$ Units are $mg\cdot kg^{-1}$.

1979). This aluminum may be soil-derived (Eisenreich et al. 1980) or it may be emitted in particulate form during coal combustion and ore smelting (Gizyn 1980; Chadwick and Lindman 1982). Practices that minimize vegetation cover and maximize erosion are frequently associated with elevated concentrations of aluminum in precipitation.

Despite high concentrations of aluminum in soils, sediments, and bedrock (see Chapter 1), concentrations in fresh water are relatively low. In near-neutral, oligotrophic waters the aluminum concentrations range from 0.002 to 0.2 $mg \cdot L^{-1}$ Al for both lakes (Table 2-2) and streams (Table 2-3). High aluminum concentrations are frequently associated with either low pH or water rich in organics (Theobald et al. 1963; Gjessing et al. 1976; Scheider et al. 1978; Johnson 1979; Hultberg and Wenblad 1980; Hutchinson 1980; Vangenechten and Vanderborght 1980).

Maximum values for aluminum approach 1.0 $mg \cdot L^{-1}$ in acidic, oligotrophic lakes in the United States, Scotland, Sweden, and Norway (Dickson 1980; Schofield and Trojnar 1980); 2.0 $mg \cdot L^{-1}$ in shallow, acidic wells in Sweden (Hultberg and Wenblad 1980); 10 $mg \cdot L^{-1}$ in acidic bog lakes in Belgium (Vangenechten and Vanderborght 1980); 250 $mg \cdot L^{-1}$ in acid strip mine lakes in the United States (King et al. 1974); and 1000 $mg \cdot L^{-1}$ in fumigated acidic ponds at the Smoking Hills, Canada (Havas and Hutchinson 1983) (see Figures 2-1 and 2-2).

Evidence that aluminum is leached from soils at low pH is based on observations in the field and experiments with water in contact with soil. Leachate experiments, using a variety of soil columns and lysimeters, have been conducted to determine aluminum mobilization under different environmental conditions. These experiments indicate that aluminum is leached more readily from acidic soils or from soils exposed to acidic precipitation than from near-neutral to alkaline soils exposed to "normal" (pH 5.5) rainwater (Bjor and Teigen 1980; Dickson 1980; Hutchinson 1980).

Field observations also indicate that acidic rainwater mobilizes aluminum from soils and sediments, and causes high aluminum concentrations in the leachate. Cronan and Schofield (1979) observed a 10-fold increase in the aluminum concentration in percolate (0.486 $mg \cdot L^{-1}$) and spring water (0.603 $mg \cdot L^{-1}$) compared with throughfall (0.045 $mg \cdot L^{-1}$). A greater than 30-fold increase was noted for stream water (0.639 $mg \cdot L^{-1}$) compared with precipitation (0.018 $mg \cdot L^{-1}$) in an acidified stream (pH 4.5) in Norway (Christophersen and Wright 1980). Concentrations of aluminum in temporary arctic ponds at the Smoking Hills following a heavy rain in June 1977 ranged from 4 to 70 $mg \cdot L^{-1}$ (Havas 1980). Precipitation and soils in this area were highly acidic (pH 2-4), as was the water in the temporary ponds (pH 2.1-3.0).

2.3 ALUMINUM SPECIATION

Aluminum can exist in a number of different forms in fresh water (see also Chapter 1). It can be suspended or dissolved. It can be bound

Table 2-2. Aluminum concentrations in surface, ground, and interstitial water.

Location		Description	pH	Total Al ($mg \cdot L^{-1}$)	Reference
Canada	Haliburton	Background levels	–	0.002-0.01	Scheider *et al*. 1979 (cited by Spry *et al*. 1981)
		n=26	5.5-6.0	0.049	
Canada	Clearwater Lake	Lake water	4.2	0.4	Dillon *et al*. 1979 (cited by Spry *et al*. 1981)
Canada	Sudbury Region, Ontario	n=5 lakes	4.0-4.6	0.28-0.38	Scheider *et al*. 1979
		n=2	5.5	0.069	
Canada	George Lake, Sudbury	Lake water	–	0.2-0.25	Gunn and Keller 1980 (cited by Kramer 1981)
Canada	Smoking Hills, N.W.T.	Temporary pools after rain, June 1977	2.25	70.0	Hutchinson 1980
			2.1	18.0	
			2.9	8.0	
			2.9	5.3	
			2.9	4.8	
			3.0	9.0	
Canada	ELA Lakes, Manitoba	Interstitial water 0-20 cm, n=16	–	<0.108-2.0	Brunskill *et al*. 1971
Canada/U.S.A.	Lake Superior	Lake water		0.001-0.026	Biesinger and Christensen 1972 (cited by Kramer 1981)
U.S.A.	Surface water	Suspended	–	3.86	Kopp and Kroner 1970 (cited by Andelman 1973); Feder 1972 (cited by Andelman 1973)
		Dissolved	–	0.074	
	+ filtration	Unfiltered	–	0.3	
		0.45-μm filtered	–	0.077	
		0.1-μm filtered	–	0.057	
U.S.A.	Lake Michigan	October 1969	–	0.015	Copeland and Ayers 1972 (cited by Andelman 1973)
		April 1970	–	0.010	
		June 1970	–	0.021	
U.S.A.	California	Surface stream	–	0.015	Silvey 1967 (cited by Andelman 1973)
		Spring	–	0.030	
		Well and oil field brine	–	0.040	
U.S.A.	Hubbard Brook, N.H.	Mirror Lake	6.6	0.005-0.02	Havas and Likens 1985
U.S.A.	Alaska	Barrow n=7	–	<0.002-0.026[a]	Brown *et al*. 1962
		Calcareous n=10	–	0.008-0.155[a]	
		Acidic n=5	–	0.031-0.131[a]	
		Lakes n=4	–	0.009-0.49[a]	
		Moraines n=4	–	0.003-0.031	
		Misc. n=4	–	0.005-0.055[a]	
U.S.A.	Colden, N.Y.	Pore water	4.9	<0.030-42.5	Hendrey and Vertucci 1980
Norway	Central	n=52 lakes	6.4	0.028±0.047	Gjessing *et al*. 1976
	Coastal	n=20	5.4	0.086±0.066	
	South-central	n=26	4.76	0.208±0.086	
	Western	n=23	5.22	0.055±0.019	
Sweden	Southern	Groundwater near S source	<5.5	0.4-1.7	Hultberg and Wenblad 1980
Scotland	Loch on Island		4.41	0.050	Wright *et al*. 1980b
	Loch Enoch		4.54	0.15	
	Loch Grannoch		4.53	0.31	
	Loch Skerrow		5.25	0.22	
	Loch Dornal		5.98	0.085	
	Black Loch		6.35	0.025	
Belgium	Moorland pools	Highly organic	3.5-8.5	0.2-8.0	Vangenechten and Vanderborght 1980
Average values	Fresh water	Median	–	0.3	Bowen 1979
		Range	–	0.008-0.0035	
	Seawater	Mean	8.2	0.002	Bowen 1979
		Range	8.2	0.001-0.0084	

---

[a] Ion-exchange resin used to concentrate cations, aluminum recovery unknown.

Table 2-3. Aluminum concentrations in stream water.

Location		Description	pH	Total Al$^{\alpha}$ (mg·L^{-1})	Reference
Canada	Various locations		-	0.050-0.14	Sorenson et al. 1974
Canada	Coniston, Ontario	Acid mine drainage from smelter	3.8	1.6	Hutchinson 1980
			3.6	<0.040	
			3.8	1.04	
			5.9	0.4	
			7.0	0.4	
			7.9	1.0	
Canada	Plastic Lake inflow	Prespring thaw	4.4-4.85	0.024-0.32	LaZerte 1984
		Spring thaw	4.3-4.38	0.15-0.25	
	Plastic Lake outflow	Prespring thaw	5.4-5.9	≤0.03	
		Spring thaw	3.49	0.10-0.12	
U.S.A.	Hubbard Brook, N.H.	Falls Brook stream 1	4.73	0.71	Johnson et al. 1981
		order 2	4.94	0.32	
		2	5.09	0.21	
		2	5.19	0.20	
		3	5.54	0.15	
		3	5.46	0.19	
		4	5.51	0.18	
		4	5.59	0.16	
		5	5.68	0.15	
		average	4.90	0.23±0.01	
U.S.A.	Colorado	Snake River	3.5-4.3	2.7-4.0	Theobald et al. 1963
		Deer Creek	8.0	0.06	
		Junction	6.8	0.6	
		Below junction	5.9	0.2	
U.S.A.	Falls Brook		5.53	0.111	Kramer 1981
	Unnamed Creek		5.63	0.054	
	Hubbard Brook	Below dam	5.72	0.29	
	Hubbard Brook	Below dam	6.10	0.066	
	Geneva Creek		6.59	0.008	
	Pumphouse Creek		6.72	0.015	
	Massey Creek		7.63	0.013	
Norway	River Ogna	August 1982	4.68-6.18	0.047-0.394	Skogheim et al. 1984

[α] Part of the variability in these values is because of different analytical techniques used and the type of sample pretreatment (i.e., filtration, etc.).

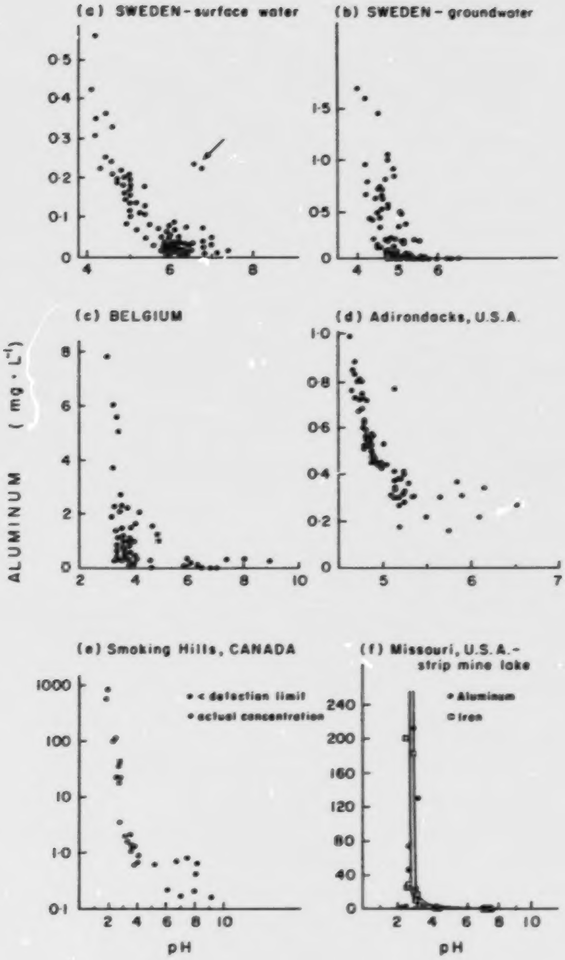


Figure 2-1. Aluminum concentrations at different pH values in various bodies of water:

(a) Swedish lakes during summer and autumn 1976 (Dickson 1980);
(b) Swedish groundwater (Hultberg and Wenblad 1980);
(c) Belgian acidic bog lakes and less acidic fishing pools (Vangenechten and Vanderborght 1980);
(d) brook in the Adirondack Mountains of New York State (Schofield and Trojnar 1980);
(e) tundra ponds at the Smoking Hills, Canada (Havas and Hutchinson 1983); and
(f) acidic strip mine lake in Missouri (King *et al*. 1974).

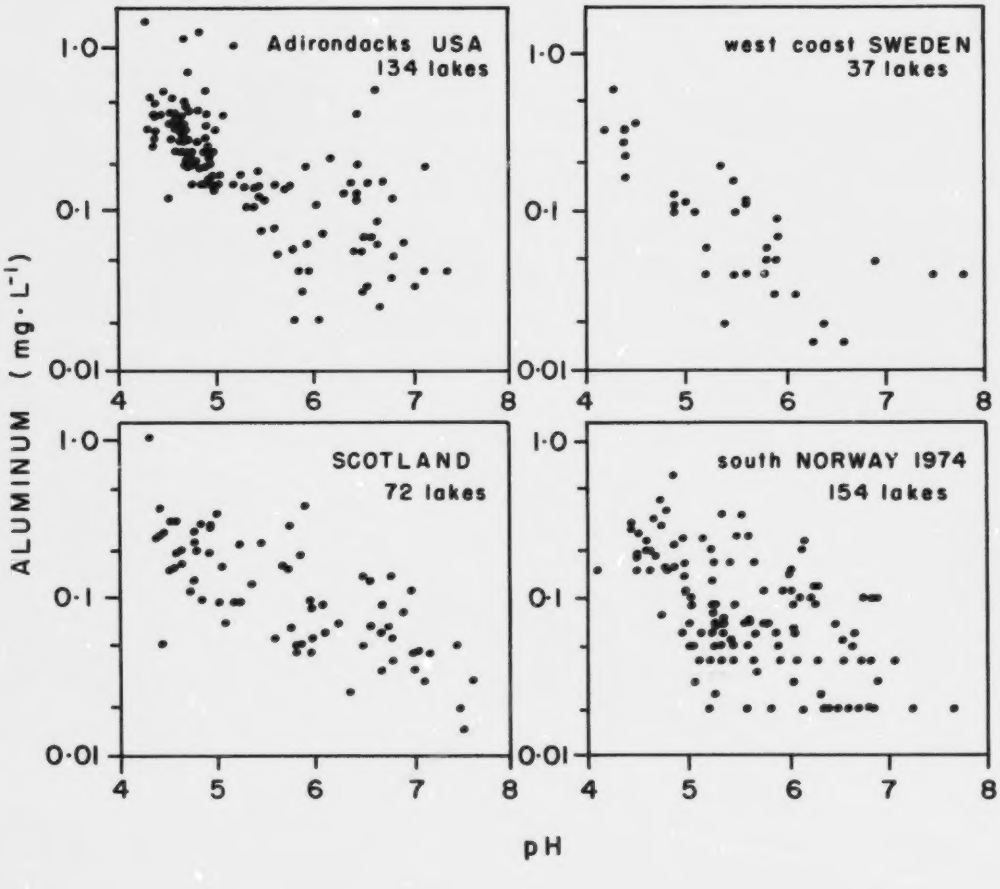


Figure 2-2. Aluminum concentrations at different pH values in freshwater lakes in the Adirondacks, Sweden, Norway, and Scotland (from Wright et al. 1980a).

with organic or inorganic ligands, or it can exist as a free aluminum ion. It can exist as a monomer in natural water, but tends to polymerize with time. Several factors determine aluminum speciation. The most important of these include: pH, dissolved organic carbon (DOC), fluoride, sulfate, and phosphate concentrations, and suspended particulates (turbidity).

2.3.1 ALUMINUM HYDROXIDE COMPLEXES

pH is one of the most important factors controlling both aluminum concentration and speciation. Aluminum concentrations increase at both high and low pH, reaching a minimum between pH 5.5 and 6.0. Between pH 4.5 and 6.5 aluminum forms hydroxide polymers (Manahan 1975). The rate of this polymerization is accelerated when the ratio of OH to Al is greater than 2 (Hem 1968a). Thus aqueous solutions of aluminum can "age" with time with subsequent changes in particle size, speciation, and solubility.

2.3.2 ALUMINUM FLUORIDE COMPLEXES

Aluminum fluoride complexes are also important in fresh water. Fluoride species range from aluminum monofluoride (AlF^{2+}) to aluminum hexafluoride ($AlF_6{}^{3-}$) as the fluoride concentration increases (Hem 1968a). In most natural waters AlF^{2+} to AlF_3 predominate.

2.3.3 ALUMINUM SULFATE COMPLEXES

Aluminum sulfate complexes tend to be less important in fresh water than those of either F or OH. The two major forms are $Al(SO_4)^+$ and $Al(SO_4)_2{}^-$ (Hem 1968a). $Al(SO_4)_x$ is present in appreciable concentrations only at low pH and high sulfate concentrations which are seldom encountered in natural water. The exceptions to this include acid mine drainage ponds, acidic volcanic lakes, acidic sulfur springs, and streams draining shale or pyrite deposits.

2.3.4 ALUMINUM PHOSPHATE COMPLEXES

Aluminum has the ability to precipitate phosphate dissolved in the water. Adsorption of orthophosphate on hydrous Al_2O_3 appears to be a function of both pH and total phosphate concentrations (Huang 1975). At 10^{-4} M PO_4 (9.5 $mg \cdot L^{-1}$), maximum adsorption occurs at pH 4.5. At lower concentrations of phosphate, which are more typical of oligotrophic lakes, maximum adsorption occurs over a broader pH range. Dickson (1980) found that maximum Al-PO_4 binding occurred between pH 5.2 and 6.0 in lake water. In the presence of high concentrations of DOC, aluminum may be preferentially bound to organics and not to phosphate (Figure 2-3). Therefore, in aluminum-contaminated water, high concentrations of DOC may increase the availability of phosphate to biota.

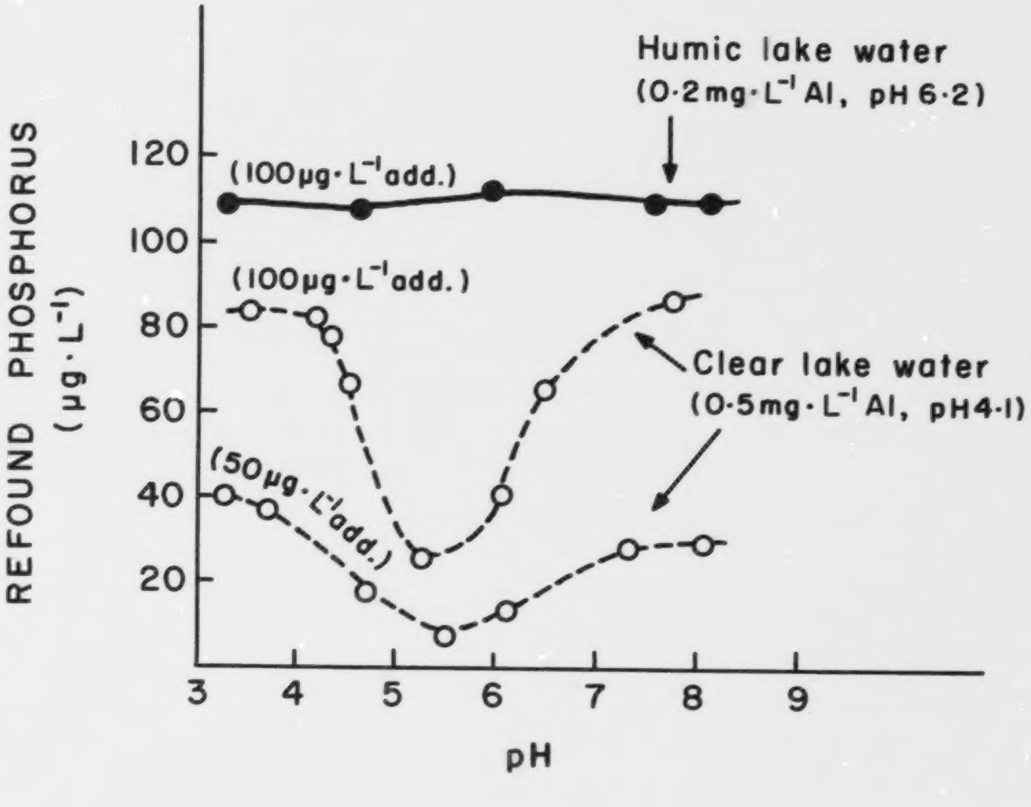


Figure 2-3. Refound phosphorus after additions of 50-100 $\mu g \cdot L^{-1}$ ortho-P to Lake Horsikan water of pH 4.1 containing 0.5 $mg \cdot L^{-1}$ Al. Also addition of 100 $\mu g \cdot L^{-1}$ ortho-P to humic lake water at pH 6.2 containing 0.2 $mg \cdot L^{-1}$ Al. pH was adjusted to different values (from Dickson 1980).

Jackson and Schindler (1975) introduced radioactively labelled orthophosphate into a lake to study the biogeochemical transformations and partitioning reactions between water and bottom mud. They found a linear relationship between total P and total Al and Fe in solvent extracts (log-log plot). Phosphorus correlated with both Al and Fe alone and together. Their interpretation was that phosphate binds to Fe and Al ions or to colloidal oxides associated with humic compounds in mud.

The consequence of Al-PO$_4$ precipitation in natural water can be considerable, because phosphate is frequently the limiting factor for photosynthesis in oligotrophic water. Many lakes which are exposed to acidic precipitation and receive aluminum from surrounding soils already have low productivity. A decrease in phytoplankton biomass and a shift from planktonic to benthic forms may be attributed, in part, to lower P concentrations. At this time, the relative effects of low concentrations of nutrients and high concentrations of H$^+$ and aluminum on primary production are not known.

2.3.5 ALUMINUM ORGANIC COMPLEXES

Aluminum concentrations in humic lakes are higher than one would predict based on pH alone (Dickson 1980). The relationship between pH and aluminum concentrations for lakes in Sweden is illustrated in Figure 2-1. The two data points that do not fit the curve (indicated by an arrow) are humic waters. Aluminum concentrations in these two lakes are 3 to 10 times higher than concentrations in clear-water lakes at the same pH. Humic and fulvic acids are known to mobilize aluminum (Malcolm and McCracken 1968, cited by Burrows 1977). Soil fulvic acid, which is a source of allochthonous water humus, complexes Fe^{3+} and Al^{3+} more strongly than divalent cations in acidic media (Schnitzer 1969, cited by Jackson 1975). The amount of organically complexed aluminum correlates well with TOC (Driscoll 1978; Driscoll *et al.* 1984; Campbell *et al.* 1984), which can vary from 0.1 to 10 mg·L^{-1} (Kramer 1981) in lakes and rivers.

2.4 ALUMINUM IN STREAMS

Concentrations and speciation of aluminum in stream water vary both spatially and temporally.

2.4.1 CONCENTRATIONS

Johnson *et al.* (1981) examined the neutralization of acidic precipitation (pH 4.14) as well as aluminum chemistry and chemical weathering in Falls Brook at the Hubbard Brook Experimental Forest, New Hampshire. They found that the upper reaches of the stream had lower pH (pH 4.73 vs. 5.68) and more aluminum (0.71 vs. 0.15 mg·L^{-1}) than the lower reaches. They hypothesized that neutralization of acidic precipitation is a two-step process at the Hubbard Brook Site. In the first step, hydrogen ions are neutralized by the dissolution of aluminum in the soil zone (gibbsite). This occurs rapidly and causes elevated aluminum concentrations in surface waters of first-order streams. In the second step, hydrogen and aluminum ion acidity is neutralized by chemical weathering of silicate minerals, dissolving primarily alkali and alkaline earth metals from bedrock and glacial till. This neutralization reaction, which is associated with third- and higher-order streams, occurs more slowly and is associated with higher pH and lower aluminum concentrations. Headwater streams, therefore, tend to be more acidic and to have more aluminum and less alkaline earths upstream than downstream. The only exception to this occurs when the soil cover along the length of a stream is not uniform. In areas of exposed bedrock, aluminum concentrations may be quite low despite low pH (Johnson et al. 1981).

2.4.2 SPECIATION

Upstream at the Hubbard Brook site, most of the aluminum was present as monomeric inorganic aluminum. Downstream the amounts of inorganic and organic monomeric aluminum were about equal (Figure 2-4a). A more detailed chemistry of the inorganic complexes is provided in Figure 2-5. This figure shows that Al-F complexes are relatively uniform along the length of the stream despite significant fluctuations in both total F and free F (Figure 2-4b). $Al(OH)_x$, $AlSO_4$, and free aluminum concentrations were highest upstream but decreased rapidly to very low levels downstream (Figure 2-5). $Al(SO_4)_x$ concentrations were at least an order of magnitude lower than either $Al(OH)_x$ or free aluminum ion concentrations and are relatively unimportant in these low sulfate waters.

2.4.3 SEASONAL CHANGES IN ALUMINUM

The aluminum concentration in stream water is influenced by the amount of precipitation and runoff acidity, and by contact time of runoff water with soils. In general, the lower the pH the higher the aluminum (inorganic monomeric) concentration in stream water. Elevated aluminum concentrations associated with lakes during spring snowmelt are characteristic of some but not all streams. In a Swedish stream (Hultberg and Andersson 1981), aluminum concentrations reached a maximum during August, rather than during spring snowmelt. Because information on stream discharge, pH of the stream water, and dissolved organic carbon concentrations is not provided, it is difficult to explain this phenomenon.

LaZerte (1984) monitored the inflow and outflow chemistry of Plastic Lake in the Muskoka-Haliburton region of Ontario from February through May 1982. He found that the outflow from Plastic Lake during the early spring, prior to spring snowmelt, had a pH between 5.5 and 5.9, and a low rate of discharge ($<40\ L\cdot s^{-1}$). During spring thaw, which occurred near the end of April, outflow pH dropped to 4.9, stream discharge increased to $200\ L\cdot s^{-1}$, and the total aluminum concentration in the water increased from less than 40 to more than $100\ \mu g\cdot L^{-1}$.

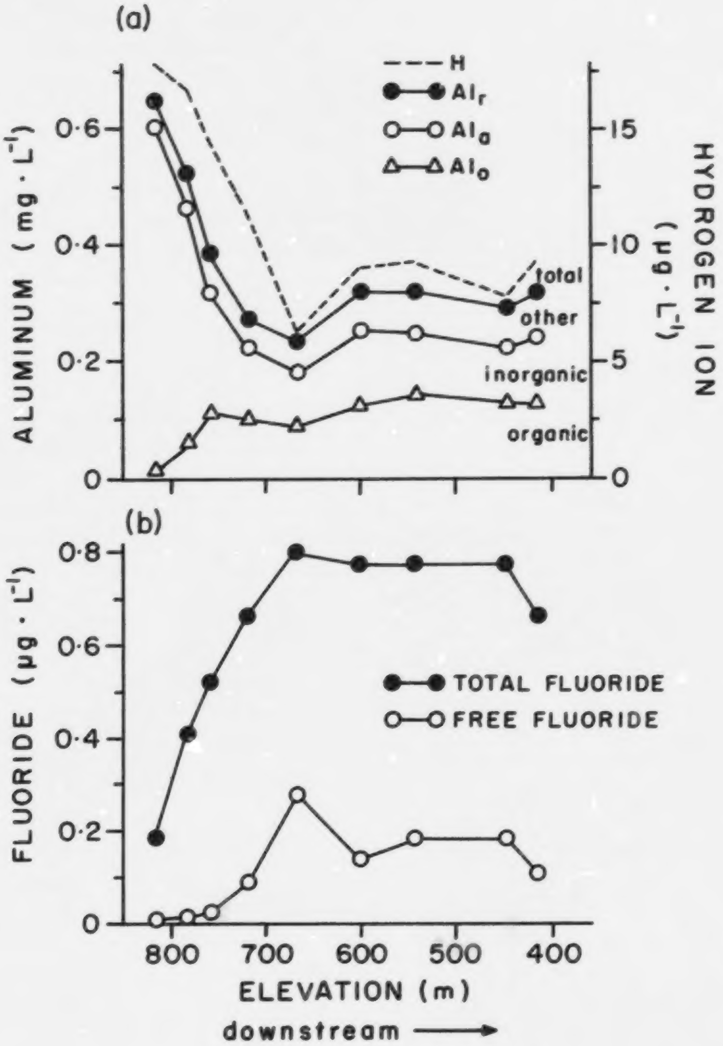


Figure 2-4. Changes in the concentrations of (a) hydrogen ions and aluminum species, and (b) total and free fluoride downstream (from Johnson et al. 1981).

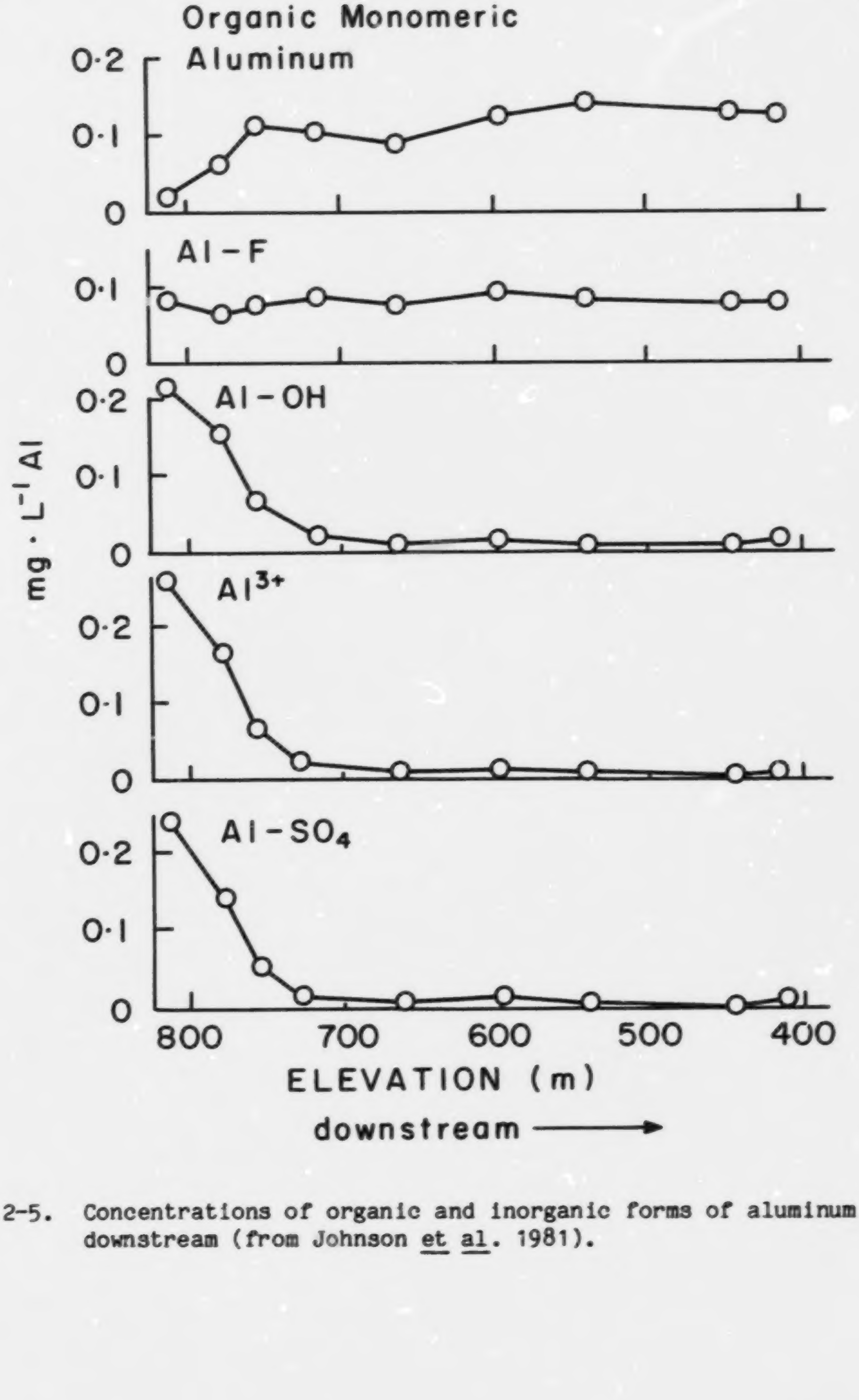


Figure 2-5. Concentrations of organic and inorganic forms of aluminum downstream (from Johnson _et_ _al_. 1981).

The inflow to Plastic Lake showed a slightly different pattern. Prior to spring thaw, the pH was much lower (<4.9) and the total aluminum concentration was much higher (250 + 100 $\mu g \cdot L^{-1}$ Al) in the inflow than in the outflow. During spring thaw the pH dropped to 4.3 but the total aluminum concentration did not change dramatically in the inflow. The only significant change was a shift from predominantly organic to inorganic monomeric aluminum. During spring thaw, both the inflow and outflow had higher inorganic monomeric aluminum concentrations, but only the outflow had higher total aluminum concentrations as well.

2.4.4 CHANGES IN ALUMINUM SOLUBILITY

Aluminum concentrations can also change dramatically at the junction of acidic and alkaline streams. Below the junction of Snake River (pH 3.5-4.3; 2.7-4.0 $mg \cdot L^{-1}$ Al) and Deer Creek (pH 8; 0.06 $mg \cdot L^{-1}$ Al) in Colorado, the pH was 5.9 and the aluminum concentration was 0.2 $mg \cdot L^{-1}$ (Theobald et al. 1963). The change in aluminum concentration was partly the result of dilution, and partly because of chemical precipitation as a result of increased pH. The white gelatinous precipitate that appeared at and below the junction consisted of ca. 60% Al_2O_3 according to the authors.

2.5 ALUMINUM IN LAKES

Aluminum concentrations and speciation in lake water can also be highly variable. The pH and total aluminum concentrations in Swedish lakes (Figure 2-6) appear to cycle, so that aluminum concentrations reach a maximum (ca. 0.7 $mg \cdot L^{-1}$) in the late winter - early spring, and a minimum (0.05-0.2 $mg \cdot L^{-1}$) in the late summer. The maximum corresponds with spring snowmelt and is paralleled by a dip in pH, whereas the minimum corresponds with fall turnover.

Seasonal changes of the major aluminum complexes for three lakes and their major tributaries in the Adirondack Mountains are illustrated in Figure 2-7. In the lakes, maximum aluminum concentrations (0.55 $mg \cdot L^{-1}$) were observed in the early spring during snowmelt (Figure 2-7). A considerable portion of the aluminum was bound by organic matter during spring thaw. Seasonal fluctuations of aluminum-organic complexes were considerable. The concentration of aluminum-organic complexes ranged from 0.03 $mg \cdot L^{-1}$ in the summer to 0.25 $mg \cdot L^{-1}$ in the spring. At least half of the inorganic aluminum was present as $Al(OH)_x$ and free Al^{3+} ions. Levels of $Al(OH)_x$ were highest (0.1 $mg \cdot L^{-1}$) in the fall, whereas those of free Al^{3+} were highest (0.13 $mg \cdot L^{-1}$) in the spring. The pH of the lake water was probably the most important single factor responsible for the different relative concentrations of free aluminum and $Al(OH)_x$ complexes. AlF_x complexes were seasonably uniform with a range of 0.1 to 0.15 $mg \cdot L^{-1}$. $Al(SO_4)_x$ complexes were relatively insignificant in these lakes because of the low sulfate concentrations in the water (less than 10 $mg \cdot L^{-1}$) (Driscoll 1978).

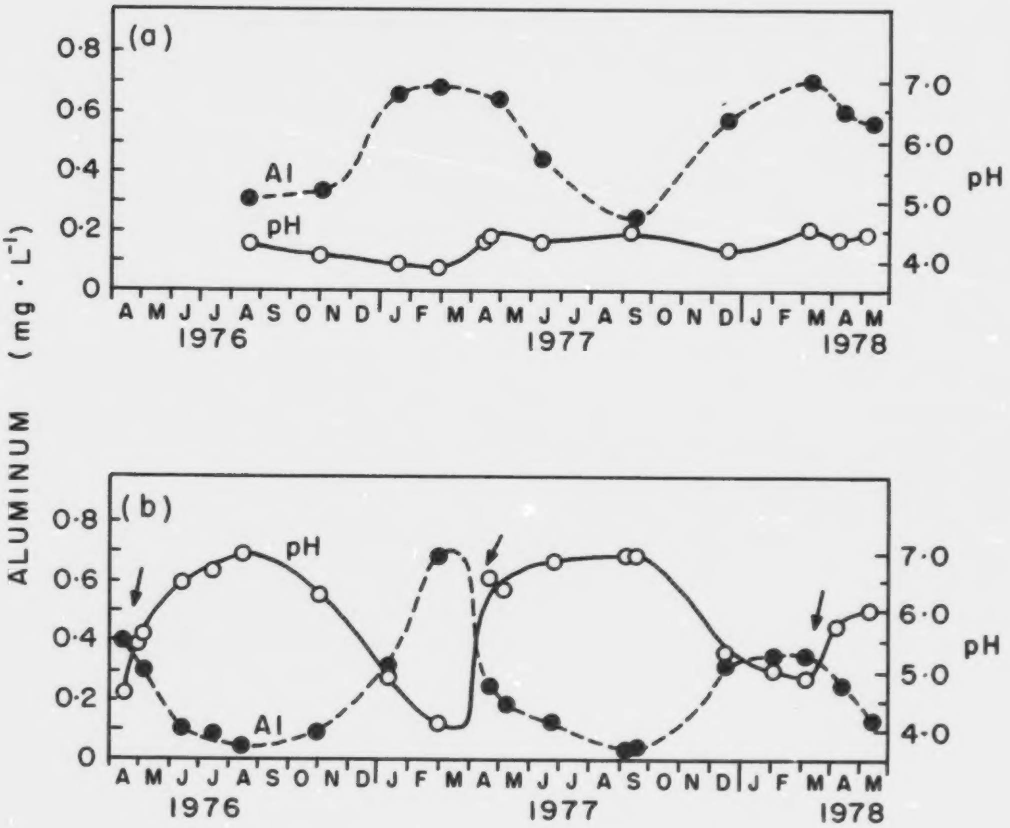


Figure 2-6. Seasonal changes in pH and aluminum in (a) Lake Horsikan, and (b) Lake Rävekärr. Arrows indicate addition of limestone (from Dickson 1978b).

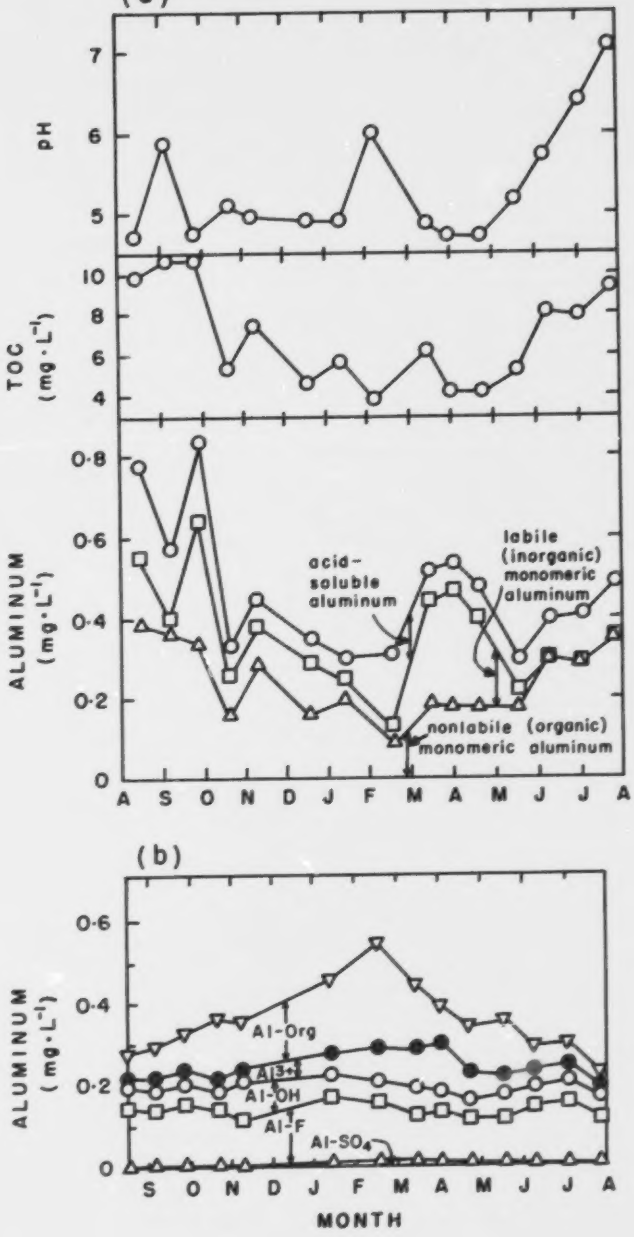


Figure 2-7. Seasonal changes in pH, total organic carbon concentrations, and aluminum speciation in rivers (a) and lakes (b) in the Adirondack Mountains (from Driscoll 1978).

Driscoll (1985) examined temporal and spatial variations of aluminum in an acidic lake in the Adirondack Mountains of New York. Monomeric aluminum concentrations were between 0.34 and 0.40 $mg \cdot L^{-1}$, and did not vary with depth during the spring or fall turnovers. During winter stratification, aluminum concentrations were 0.54 $mg \cdot L^{-1}$ immediately under the ice and decreased to 0.28 $mg \cdot L^{-1}$ at greater depth. This pattern was reversed during the summer months, with minimum aluminum concentrations in the epilimnion. The seasonal and spatial patterns for inorganic monomeric aluminum were similar.

2.6 ALUMINUM AS A BUFFER

Aluminum silicate acts as a buffer when it is dissolved in acidic soils. Similarly, aluminum (and iron) dissolved in water acts as a weak acid (Dickson 1978a). Acidic lakes with elevated concentrations of aluminum ions have higher acidity than is indicated by pH alone.

A titration curve for an extremely acidic pond (pH 2) containing high concentrations of aluminum (600 $mg \cdot L^{-1}$) and iron (2000 $mg \cdot L^{-1}$) showed that aluminum and iron act as buffers between pH 3.5 and 4.5. The buffering corresponds to two plateaus in the curve (Figure 2-8a). At pH 3.5 an orange precipitate formed, which consisted primarily of iron and aluminum hydroxide complexes (Havas 1980). Similarly, the amount of base needed to increase the pH from 3 to 7 (for example) was much greater for acid strip mine water (which had elevated concentrations of aluminum and other metals) than for a sulfate-adjusted solution (with no metals) (Figure 2-8b).

Dickson (1980) found that synthetic lake water, to which aluminum was added (0.5 $mg \cdot L^{-1}$ Al), had a higher buffering capacity than the same water with no aluminum added. Titration curves were similar for an acid lake containing 0.45 $mg \cdot L^{-1}$ Al and for synthetic lake water with a comparable aluminum concentration.

The buffering capacity of aluminum between pH 3 and 6 was tested experimentally using both natural and synthetic lake water with and without organic acids (Johannessen 1980). Addition of aluminum (1 $mg \cdot L^{-1}$ Al as $Al_2(SO_4)_3$) increased the buffering capacity between pH 3.0 and 5.5 in synthetic water (low organics) by 105 $\mu eq \cdot L^{-1}$, and in humic water by 74 $\mu eq \cdot L^{-1}$. The presence of organic acids in this experiment reduced the buffering capacity of aluminum by 30%, presumably by complexation with aluminum. According to Johannessen (1980), aluminum acted as a buffer between pH 4.0 and 5.0 in these experiments. A calculation of the relative contribution of aluminum and organic substances to buffering indicated that aluminum contributed 7.5 $\mu eq \cdot L^{-1}$ per milligram organic carbon to the buffering capacity.

The above discussion on the role of aluminum as a buffer suggests that if hydrogen ions are no longer added to lakes, the rate of "recovery" (i.e., a return to the original pH) should be a function of free aluminum concentrations. Theoretically, the higher the free aluminum concentration the slower the recovery is likely to be.

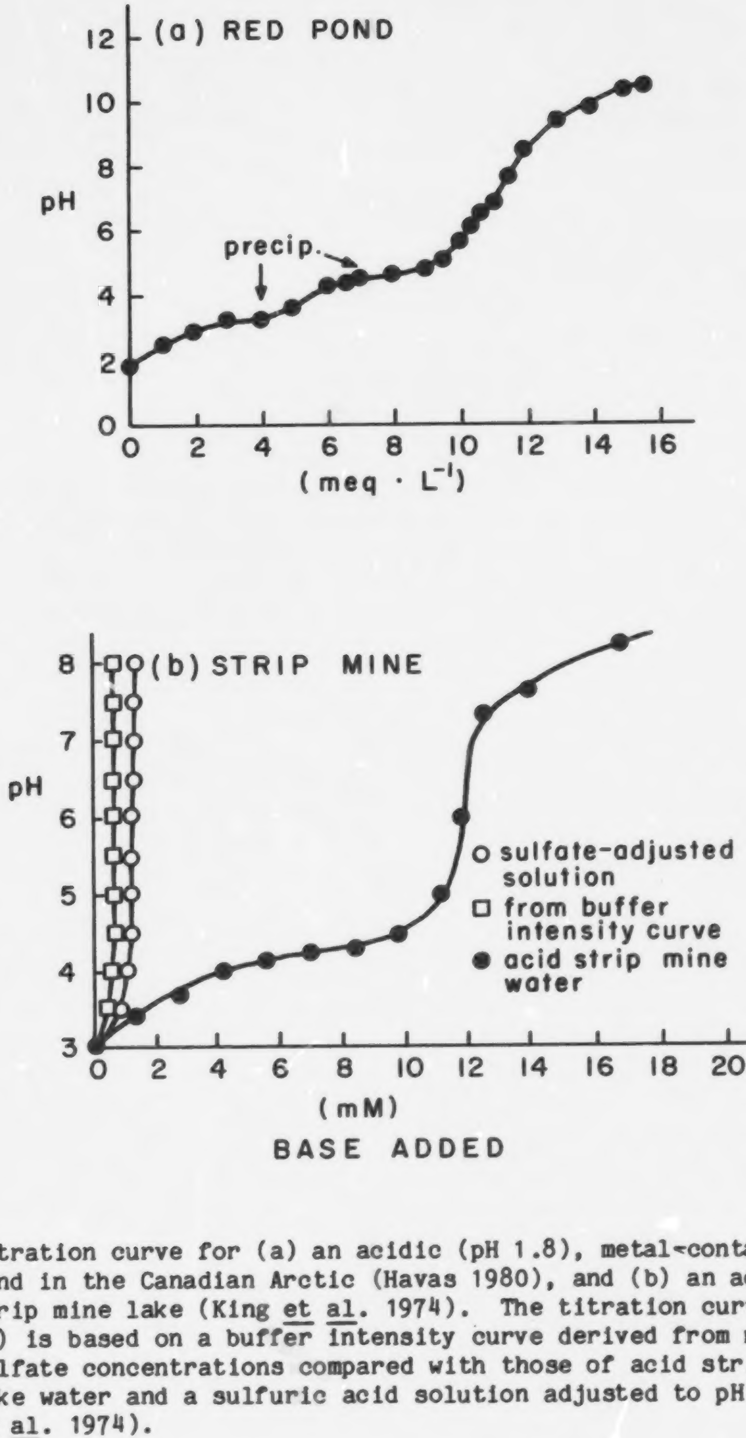


Figure 2-8. Titration curve for (a) an acidic (pH 1.8), metal-contaminated pond in the Canadian Arctic (Havas 1980), and (b) an acid strip mine lake (King et al. 1974). The titration curve in (b) is based on a buffer intensity curve derived from measured sulfate concentrations compared with those of acid strip mine lake water and a sulfuric acid solution adjusted to pH 3 (King et al. 1974).

2.7 ALUMINUM BUDGET

An input-output budget for Birkenes watershed in S.E. Norway indicated a net loss of Al, Ca, and Mg; a net gain of H, K, NH_4, and NO_3; and a balance between input and output for Cl (assumed), Na, and SO_4 (Gjessing et al. 1976). A breakdown of aluminum dynamics showed that total aluminum input was 2.4 $keq{\cdot}km^{-2}{\cdot}a^{-1}$ (of which 1.4 $keq{\cdot}km^{-2}{\cdot}a^{-2}$ was wet input), whereas output was 33 $keq{\cdot}km^{-2}{\cdot}a^{-1}$ (out/in = 14). The results for Fyresdal/Nissedal area in Norway (Johannessen and Joranger 1976, cited by Gjessing et al. 1976) and for three lakes in the Adirondack region of New York (Hendrey et al. 1980) also indicate a net loss of aluminum from the watershed. The net loss of Ca, Mg, and Al is a function of natural weathering, which appears to be accelerated by acidic precipitation (see Chapter 4 for additional information on aluminum weathering).

2.8 FIELD EXPERIMENTS

2.8.1 ACIDIFICATION

Experimental manipulations of lakes and streams have added considerably to our understanding of acidification and its effect on aluminum dynamics. Two acidification studies will be considered in detail.

The first of these studies examined the effect of acidification of Lake 223, located in the Experimental Lakes Area (ELA) of Northwestern Ontario (Schindler et al. 1980b). In 1976 the pH of this lake was between 6.7 and 7.0. Each year the pH was lowered 0.5 pH units by weekly additions of sulfuric acid during the ice-free period. As a result of the acidification, the mean annual concentration of aluminum increased from 0.006 $mg{\cdot}L^{-1}$ in 1976 to 0.026 $mg{\cdot}L^{-1}$ in 1978 (Table 2-4; Harvey et al. 1981). The concentrations of Zn, Mn, and Fe also increased during this period.

In a complementary study, designed to determine the effect of pH on metal release and sorption by sediments, large enclosures were sealed into the sediments of Lake 223 (Schindler et al. 1980a). The pH within these enclosures was adjusted with H_2SO_4 to pH 6.7-6.8 (control), pH 5.7, or pH 5.1. Compared with the control, concentrations of Mn, Zn, and Fe were higher in the water column at pH 5.1 and 5.7, whereas aluminum concentrations were elevated only in the pH 5.1 enclosure. Concentrations of aluminum in the control and at pH 5.7 were between 0.002 and 0.005 $mg{\cdot}L^{-1}$. At pH 5.1, aluminum concentrations ranged from 0.009 to 0.014 $mg{\cdot}L^{-1}$. The most likely source of metals in both the enclosure experiment and the lake acidification experiment is the sediment, as neither the watershed soils nor the rocks were acidified.

The second study examined the effects of acidification of a portion of Norris Brook in the Hubbard Brook watershed. This small stream was experimentally acidified with H_2SO_4 to pH 4.0, which was maintained at

Table 2-4. Mean annual concentrations of Al, Zn, Mn, and Fe in Lake 223 during the first 3 years of acidification (from Harvey *et al.* 1981).

Year	Concentrations ($\mu g \cdot L^{-1}$)				
	Al	Zn	Mn	Fe	pH[α]
1976	6.1	2.0	13.8	19.2	6.7-7.0
1977	14.4	3.5	45.3	50.2	6.0-6.2
1978	26.1	3.2	88.5	49.3	5.7-5.9

[α] From Schindler *et al.* 1980b.

source from April to September 1977 (Hall et al. 1980). Water was analyzed at an upstream reference site and at a site 120 m below the point of acidification. Concentrations of Al, Ca, and, to a lesser extent, Mg and K increased in the stream water at pH 4 (Figure 2-9). Aluminum concentrations were, on average, 0.15 $mg \cdot L^{-1}$ higher in the acidified water. Acidification had no appreciable effect on either Na or DOC or on the concentrations of NO_3, NH_4, Ni, Pb, Cu, and Zn (not presented in Figure 2-9). Once again, the sediments are the most likely source of these elements.

2.8.2 LIMING

The effect of liming on water quality in acidified water has been studied in both Europe and North America (Table 2-5). Concentrations of aluminum and other trace metals are usually reduced after neutralization (Yan et al. 1977; Dickson 1980; Hultberg and Andersson 1981). If high pH is not maintained by regular liming, the hydrogen ion and aluminum concentrations tend to increase (Dillon et al. 1979).

The effect of liming on seasonal aluminum concentrations in stream water is presented in Figure 2-10 (Hultberg and Andersson 1981). Addition of lime to stream water significantly decreased the concentration of aluminum (from 0.7 to 0.2 $mg \cdot L^{-1}$). The pH of the stream water before and after liming was not given. However, the pH of Lake St. Holmevatten, into which the stream discharges, increased from 4.5 to 7.5. Therefore, whereas acidification increases aluminum concentrations in fresh water, liming has the opposite effect.

Liming changes not only aluminum concentrations but also aluminum speciation. In some cases aluminum can become more toxic in lakes that are limed. This increase in toxicity may have devastating effects on fish populations and other biota (see Chapter 3).

2.8.3 ALUMINUM ADDITIONS

In an attempt to simulate an episodic increase in the aluminum concentrations during acidic snowmelt, $AlCl_3$ was added to a second-order reach of Norris Brook, in the Hubbard Brook Experimental Forest (Hall et al. 1985). Aluminum concentrations were experimentally elevated in a stepwise fashion at hourly intervals for a total of 5 h. Experimental aluminum concentrations in the water varied from 0.28 to 2.5 $mg \cdot L^{-1}$. These concentrations were significantly higher than the pre-experimental concentration of 0.012 $mg \cdot L^{-1}$.

Adding aluminum significantly decreased the pH of the stream water in a stepwise fashion, from the original 6.4 to a minimum 4.85 after 5 h. Dissolved organic carbon concentrations also decreased, from 1.4 to approximately 0.9 $mg \cdot L^{-1}$ following the first addition, and remained relatively constant for the duration of the experiment.

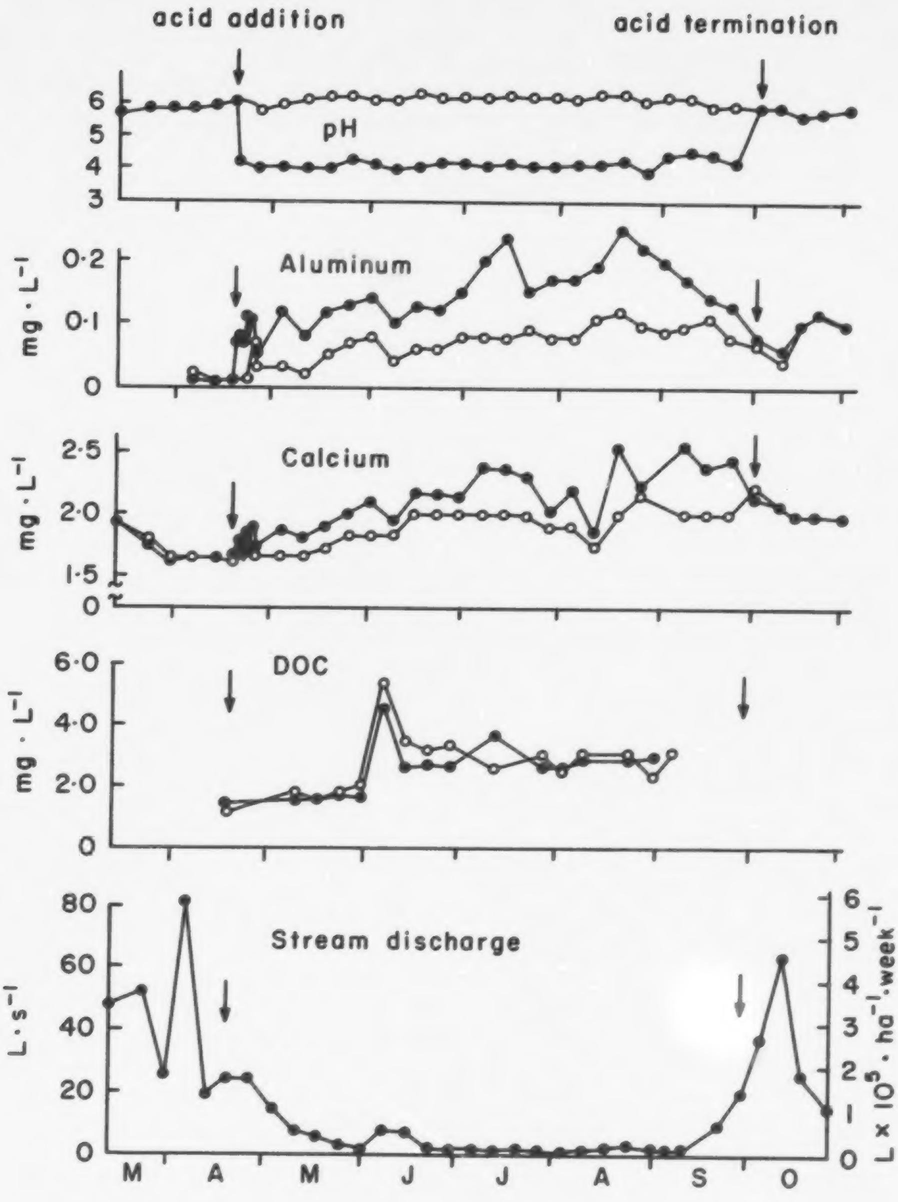


Figure 2-9. Seasonal changes in aluminum, calcium, and dissolved organic carbon concentrations, pH, and stream discharge in Norris Brook, New Hampshire. Solid circles are immediately downstream from acid addition site. The reference portion of the stream (open circles) is 120 m above acid addition (from Hall _et al_. 1980).

Table 2-5. Chemical changes associated with liming.

Location	Lake	Chemical changes before and after liming							Reference
Canada	Lodhi near Sudbury		PRELIMING		POSTLIMING				Dillon *et al.* 1979 (cited by Harvey *et al.* 1981)
		Year	1973	1974	1975	1976	1977	1978	
		pH	4.39	6.04	6.09	5.27	5.27	4.79	
		Al ($\mu g \cdot L^{-1}$)	--	140	110	120	100	160	
		Cu ($\mu g \cdot L^{-1}$)	84	44	43	37	44	71	
Canada	Nelson	LIME ADDITION	BEFORE	AFTER	% DIFFERENCE				Yan *et al.* 1977
		Alkalinity ($mg \cdot L^{-1}$)	2.5	3.8	+ 49%				
		pH	5.7	6.4	- 80%				
		Al ($\mu g \cdot L^{-1}$)	81	13	- 84%				
		Mn "	63	18	- 71%				
		Fe "	61	19	- 69%				
		Ca ($mg \cdot L^{-1}$)	4.06	5.41	+ 33%				
Sweden	Laxforsen fishfarm	LIME ADDITION	BEFORE	AFTER	% DIFFERENCE				Dickson 1980
		pH	4.75	6.32	- 97%				
		Al-TOTAL ($\mu g \cdot L^{-1}$)	288	233	- 19%				
		-<0.01 µm ($\mu g \cdot L^{-1}$)	184	65	- 65%				
Sweden	stream limed	LIME ADDITION	BEFORE	AFTER	% DIFFERENCE				Hultberg and Andersson 1981
		Lake pH	4.5	7.5	+100%				
		Al ($\mu g \cdot L^{-1}$)	500	<100	- 80%				

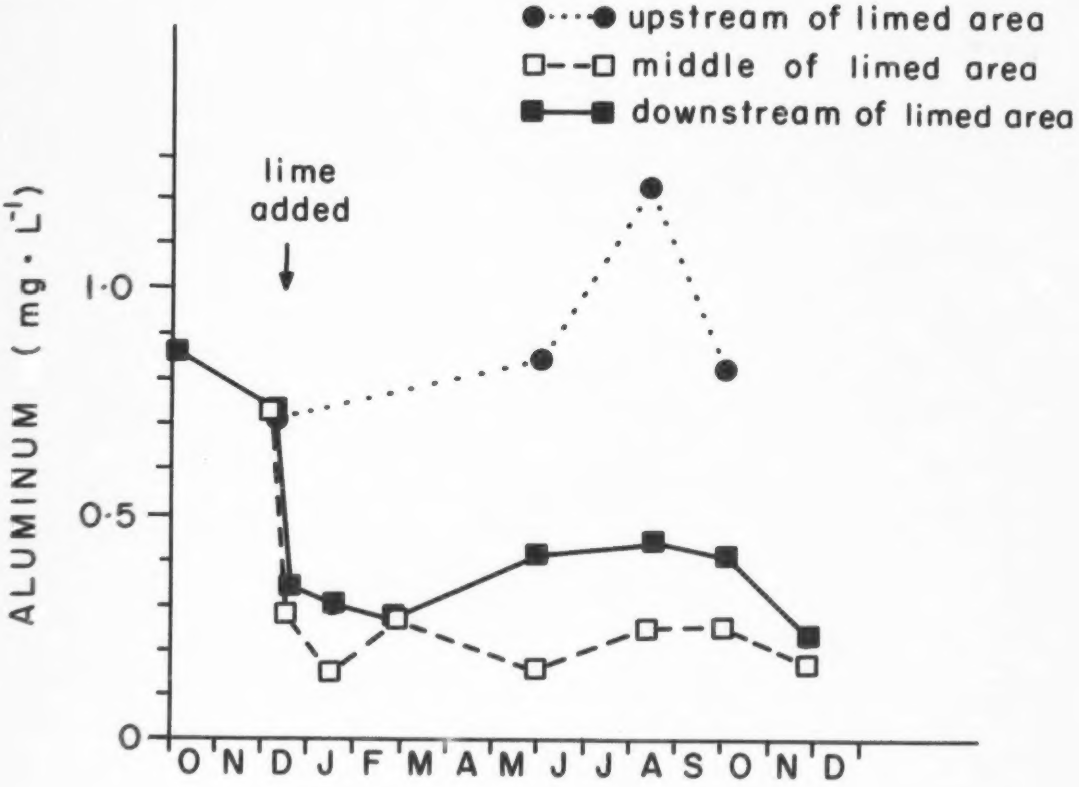


Figure 2-10. Effect of liming on seasonal aluminum concentrations in stream water (from Hultberg and Andersson 1981).

There was a discrepancy between the amount of aluminum added and the amount measured in the water. A follow-up laboratory study using Norris Brook water corroborated many of the chemical changes observed in the field and suggested that the discrepancy was largely the result of removal of aluminum from solution by adsorption onto suspended particles and, to a lesser degree, uptake by the stream bed.

The production of foam in the reach receiving aluminum was noted and attributed to a decrease in surface tension caused by hydrophobic colloidal particles on which aluminum and then dissolved organic carbon had adsorbed. Changes in surface tension could have a profound impact on biota, which live at or near the water/air interface, as well as on those species that have an emergent phase in their life cycle, if movement from the water to the air is hindered.

The effect of aluminum on the biota was also monitored. Rate of invertebrate drift, which may be an avoidance reaction, increased dramatically. During the first few hours of the experiment, invertebrates associated with the surface film drifted in greatest numbers; this was attributed to changes in surface tension. Drift of immature insects reached a maximum after 4 h, and was likely the result of toxic levels of both aluminum and hydrogen ions.

2.9 ACID MINE DRAINAGE

Acid mine drainage and waters draining acidic shales constitute a special type of environment. Chemically they are considerably more acidic and have considerably higher concentrations of aluminum and other metals than do lakes and streams affected by acidic precipitation. Biologically they have a restricted but characteristic flora and fauna.

The pH of acid mine water may be less than 2, but usually ranges from 3 to 4.5 (Parsons 1968; Warner 1971). The relationship between pH and aluminum is similar to that observed in acidified lakes and streams (Figures 2-1a to d and 2-2). However, aluminum concentrations are frequently higher than 1 $mg \cdot L^{-1}$ and can be as high as several hundred milligrams per litre (King _et_ _al_. 1974) (Figure 2-1f).

As previously mentioned, both aluminum and iron salts act as buffers at low pH. A titration curve for an acid strip mine lake differs considerably from that for a sulfuric acid solution adjusted to the same pH, but resembles the titration curve for an acidic pond containing high concentrations of aluminum and iron (Figure 2-8).

The presence of elevated aluminum and iron concentrations reduces the rate of recovery of acid mine drainage water. Recovery of four acid mine lakes in Missouri was studied by Campbell _et_ _al_. (1964). Within 23 years (1940-1963), the pH increased from 2.9 to 4.0 in one lake, and from 3.8 to 7.3 in another. Recovery was also characterized by a decrease in the concentration of iron and other metals (Campbell et al. 1964; King et al. 1974).

The increase in pH is not a linear function with time. Below pH 4.5 the pH increases slowly, because of the presence of aluminum and iron, which act as buffers in the pH range 2.5 to 4.5 (King et al. 1974). Once the pH exceeds 4.5, it continues to increase rapidly (Figure 2-8b) until the bicarbonate buffering plateau is reached at pH 7-8. Consequently there are few acid mine waters with a pH between 4.5 and 6.0.

A number of chemical transformations occur during recovery. Some of the more important ones are summarized in Figure 2-11. Sulfate is reduced to hydrogen sulfide with the production of bicarbonate, according to the following equation (King et al. 1974):

$$SO_4^{2-} + 2C_{org} + 2H_2O \xrightarrow{\text{bacteria}} H_2S(g) + 2HCO_3^- \qquad [2\text{-}1]$$

Organic matter speeds up this process. As the pH increases, aluminum precipitates as $Al(OH)_3(s)$, whereas iron precipitates either as $Fe(OH)_3(s)$ or as FeS.

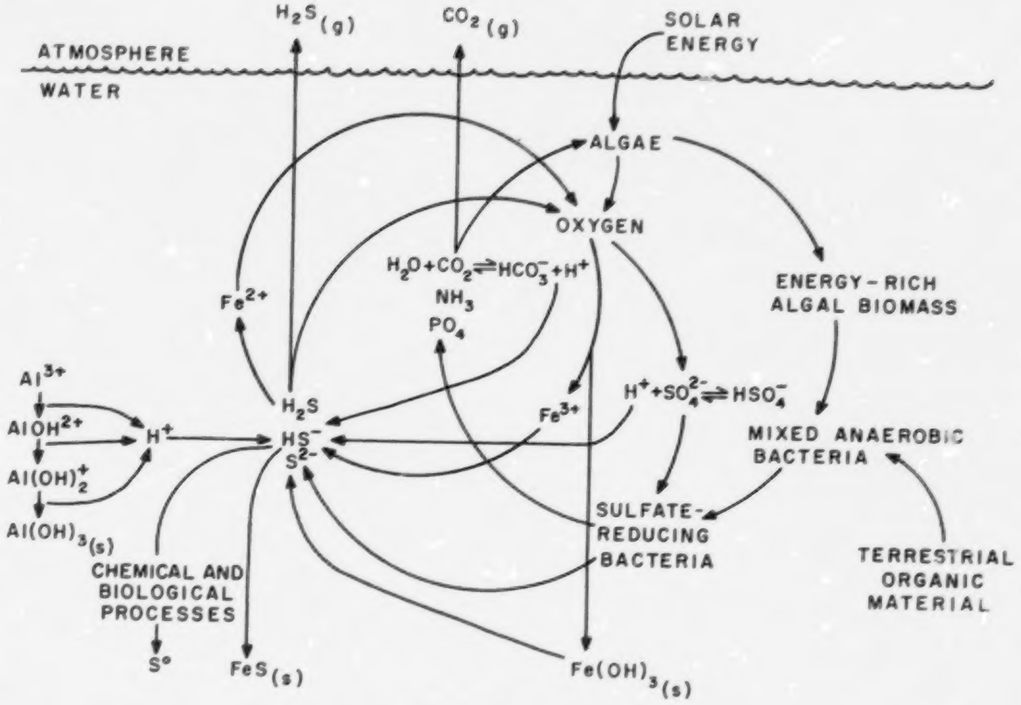

$H_2S_{(g)}$
$CO_{2\,(g)}$
SOLAR ENERGY
ATMOSPHERE
WATER
ALGAE
OXYGEN
$H_2O+CO_2 \rightleftharpoons HCO_3^- + H^+$
NH_3
PO_4
ENERGY-RICH ALGAL BIOMASS
Fe^{2+}
Al^{3+}
$AlOH^{2+}$
$Al(OH)_2^+$
$Al(OH)_{3(s)}$
H^+
H_2S
HS^-
S^{2-}
Fe^{3+}
$H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-$
MIXED ANAEROBIC BACTERIA
SULFATE-REDUCING BACTERIA
TERRESTRIAL ORGANIC MATERIAL
CHEMICAL AND BIOLOGICAL PROCESSES
S°
$FeS_{(s)}$
$Fe(OH)_{3(s)}$

Figure 2-11. Processes involved in acid strip mine lake recovery (from King _et_ _al_. 1974).

3.0 EFFECTS OF ALUMINUM ON AQUATIC BIOTA

Magda Havas

Institute for Environmental Studies
University of Toronto
Toronto, Ontario M5S 1A4

3.1 INTRODUCTION

The relatively recent interest in aluminum in the aquatic environment can be attributed largely to its harmful effects on aquatic organisms. Aluminum concentrations that are currently found in some acidified lakes and streams are known to be toxic to a variety of species. Because aluminum is present in all soils and sediments and is readily leached at low pH, it will remain a problem as long as lakes and streams continue to acidify.

This section will review some of the recent studies on the effects of aluminum on aquatic biota. During the later stages of writing this chapter it was learned that a number of studies dealing with the effects of aluminum on aquatic organisms were still in progress. Data from some of this unpublished work were kindly provided to the author and are included in this chapter. A list of these unpublished studies as well as those which arrived too late to be included in this chapter are provided in Appendix III.0.

3.2 AQUATIC MOSSES AND MACROPHYTES

The effects of aluminum on aquatic macrophytes are poorly understood. Because aluminum can be toxic to terrestrial vegetation it is likely to have a similar effect on aquatic vegetation. With the continued mobilization of aluminum in regions receiving acidic rain, the effects of aluminum may become quite pronounced. Mosses and macrophytes are important components of the aquatic ecosystem. They play a significant role in nutrient cycling and in shoreline stabilization. They provide a microhabitat for both plants and animals, as well as food for land animals, including deer and moose. Changes in their distribution, abundance, and chemical makeup may have far-reaching consequences to both aquatic and terrestrial ecosystems.

Several studies (Miller _et al_. 1983; Wile and Miller 1983; Roberts and Singer 1983 (Appendix III.0); Roberts _et al_. 1985 (Appendix III.0)) have examined the distribution of aquatic mosses and macrophytes in acidic and circumneutral lakes. Although some characteristic changes in plant communities in acidic lakes have been reported, it is not clear if these are the result of toxicity of hydrogen ions, toxicity of increasingly available metals, reduced nutrient availability (PO_4 and HCO_3), and/or competitive exclusion. Aquatic plants that occur at low pH (with presumably elevated aluminum concentrations) are listed in Table 3-1. The relative importance of aluminum in determining species composition and abundance in these environments is not yet known.

Roberts *et al.* (1985) surveyed submerged macrophyte communities in lakes ranging in pH from 6.9 to 4.4 in the Adirondack Region of New York State. They found that below pH 5.5 there was a decrease in species richness and species diversity. The lakes below pH 5.5 had concentrations of aluminum between 0.24 and 0.30 $mg\cdot L^{-1}$. Several species were common to all the lakes (*Utricularia purpurea*, *U. resupinata*, *Eriocaulon septangulare*, *Myriophyllum tenellum*, and *Lobelia dortmanna*), whereas others were found only in the acidic lakes (*Utricularia geminiscapa*, *Potamogeton confervoides*, and various *Sphagnum* species). In a similar New Hampshire survey, Roberts and Singer (1983) found that *Eriocaulon septangulare* and *Scirpus subterminalis* were common.

Wile and Miller (1983) studied 46 soft-water lakes in Ontario (i.e., Sudbury, Killarney, Haliburton, Muskoka, and Parry Sound) which ranged in pH from 7.1 to 3.3. They found that acidified lakes with low concentrations of trace metals were able to support a diverse flora. Only metal-contaminated lakes, particularly those around Sudbury, had fewer species than normal. The species that were able to tolerate both metal-contaminated and acidified conditions included: *Pohlia nutans* (terrestrial moss), *Cladopiella* (?) *fluitans*, *Sparganium* sp., *Eleocharis acicularis*, *Nuphar varigatum*, *Sagittaria* sp., *Juncus peliocarpus*, and *Drepanocladus exannulatus*. Many more species were found below pH 5.0 in lakes not contaminated with metals.

There is little information on aluminum concentrations in aquatic macrophytes, and, unfortunately, even some of these data are of questionable accuracy. Aluminum concentrations for a number of different species collected from a variety of environments are provided in Tables 3-2 and 3-3. Concentrations of aluminum in aquatic plants range from less than 40 to 32 000 $\mu g\cdot g^{-1}$ (dry weight). There appear to be seasonal variations, site-to-site variations, differences in portion of the plant analyzed, and species differences (Hutchinson 1975; Gorham and Tilton 1978; Best and Peverly 1981; Miller *et al.* 1983).

Pajos (1984; Appendix III.0) examined the chemical composition of aquatic macrophytes collected from nine lakes in south-central Ontario. Aluminum concentrations in these lakes ranged from 0.03 to 0.37 $mg\cdot L^{-1}$ (Table 3-3). Although the aluminum concentrations in the macrophytes were highly variable, it appears that concentrations were considerably higher in submergent portions of monocots than in emergent portions. This correlation was not obvious among the two dicots analyzed (Table 3-3). The correlation between the aluminum contents of macrophytes and water was not significant for any of the species analyzed.

The aluminum content of aquatic mosses and macrophytes collected from tundra ponds at the Smoking Hills, N.W.T., was determined (Havas 1986). Pond water, in which aquatic plants were found, ranged from pH 2.66

Table 3-1. Relative abundance of aquatic mosses and macrophytes in clear-water acidic environments (≤ pH 5.6).[a]

Plant	Present at low pH (potential acid/Al "tolerant" species)
BRYOPHYTES (mosses)	*Bryum* sp.
	Campylium polyganum
	Drepanocladus exannulatus
	Fontinalis sp.
	Leptodictyum riparium
	Lophozia obtusa
	Pogonatum urnigerum
	Polytrichum longisetum
	Sphagnum cuspidatum
	S. pylaesii
	S. subsecundum v. *contortum*
	S. subsecundum v. *platyphylum*
SPERMATOPHYTA (seed-bearing plants) MONOCOTS	*Carex aquatilis*
	C. rostrata
	Eleocharis acicularis v. *submerse*
	E. robbinsii
	Eriocaulon septangulare
	Eriophorum angustifolium
	Glyceria fluitans
	Juncus bulbosus
	J. effusus
	J. fluitans
	J. militaris
	J. pelocarpus
	Phragmites australis (communis)
	Potamogeton confervoides
	Scirpus subterminalis
	Sparganium erectum
	S. simplex
	Typha latifolia
DICOTS	*Brasenia schreberi*
	Litorella americana
	Litorella spp.
	Lobelia dortmanna
	Lycopus spp.
	Myriophyllum farwelli
	M. tenellum
	Nuphar variegatum
	Nymphaea odorata
	Nymphoides cordatum
	Polygonum amphibium
	Pontederia cordata
	Utricularia geminiscapa
	U. purpurea
	U. resupinata
	U. vulgaris

---

[a] Sources: Lackey 1938; Gorham and Gordon 1963; Grahn *et al*. 1974; Hultberg and Grahn 1975; Hendrey *et al*. 1976; Grahn 1976, cited by Harvey *et al*. 1981; Sand-Jensen and Rasmussen 1978; Nilssen 1980; Hendrey and Vertucci 1980; Havas 1980; Roberts and Singer 1983; Wile and Miller 1983.

Table 3-2. Aluminum concentrations in aquatic macrophytes.

Location	Lake	pH	Al in water sediments[α, β] (μg·g⁻¹)	Species	Al in plant[γ] (μg·g⁻¹)	Plant part	Reference
Canada	Clearwater	4.4	7300[α] ± 1500	*Eriocaulon septangulare*	4100 ± 700[δ]	Root	Miller *et al.* 1983
					3800 ± 800	Shoot	
	Harp/Red	6.5	-	"	2900 ± 600	Root	
	Chalk Lake	-	2600 ± 400	"	2000 ± 500	Shoot	
				Eleocharis acicularis	600-7800	ns[η]	
				Eriocaulon septangulare	800-6800	ns	
				Fontinalis spp.	1500-18 000	ns	
				Sphagnum spp.	2900-22 000	ns	
Canada and U.S.A.	-	-	-	*Sphagnum fuscum*	517	5 cm top	Gorham and Tilton 1978
				S. magellanicum	250	Shoot	
				S. nemoreum	390	Shoot	
				S. wulfianum	1000	Shoot	
					517 ± 298 mean		
					120 - 970 range		
U.S.A.	Cedar Lake	-	-	*Nuphar advena*	230	Petiole	Cowgill 1973a (cited by Hutchinson 1975)
					510	Leaf	
					260	Fl. stalk	
					270	Flower	
	"			*Nymphaea odorata*	420	Petiole	
					730	Leaf	
					180	Fl. stalk	
					1250	Flower	
	Linsley Pond	-	-	*Nuphar advena*	300	Petiole	
					390	Leaf	
					330	Fl. stalk	
					270	Flower	
				Nymphaea odorata	180-199	Petiole	
					610-179	Leaf	
					370-188	Fl. stalk	
					1730-194	Flower	
				Potamogeton cf. *praelongus*	250		
				Ceratophyllum demersum	785		
U.S.A.	Colden	4.9	42.5[ε]	*Sphagnum pylaesii*	32 000	ns	Hendrey and Vertucci 1980
U.S.A.	-	-	-	*Sphagnum*	372-3910 range	ns	Furr *et al.* 1979
					1130 mean	ns	
U.S.A.	Coal ash effluent	Acidic	13	*Lemna*	3740[ζ]	ns	Guthrie and Cherry 1979
			40 700[β]	*Typha*	370[ζ]	ns	
				Pontederia	340[ζ]	ns	
					43[ζ]	ns	

[α] In sediments (dry weight).

[β] In sediments (wet weight).

[γ] Dry weight.

[δ] 95% confidence limit.

[ε] In pore water.

[ζ] As Al-Si (wet weight).

[η] Not specified.

Table 3-3. Concentrations of aluminum in aquatic macrophytes collected from lakes in south-central Ontario, fall, 1984 (Pajos 1984).

			Monocots						Dicots			
	Water		*Eriocaulon septangulare*		*Sagittaria latifolia*		*Sparganium eurokarpum*		*Nymphaea odorata*		*Pontederia cordata*	
Lake	pH	Al (mg•L^{-1})	E	S	E	S	E	S	E	S	E	S
Plastic	6.09	0.37	270	3 600	220	1 200	140	2 000	170	250		
George	5.78	0.28	-	14 000	800	3 500	130	1 700	420	140	260	110
Joe	6.42	0.23	-	4 900	-	-	180	740	400	420	-	-
Crane	6.87	0.22	-	7 000	100	6 200	90	150	70	<5	50	<10
Crosson	6.01	0.15	-	400	-	-	90	50	120	150	<8	65
Carlyle	6.08	0.13	-	400	-	-	110	1 800	100	80	40	40
Mountain	7.21	0.11	-	300	40	7 100	-	-	70	50	-	-
Blackstone	7.22	0.10	230	12 000	690	13 000	140	830	200	380	60	370
Horseshoe	7.07	0.03	230	6 200	-	-	-	-	100	50	110	80

Note: Values for emergent (E) and submergent (S) portions are provided.

and 90 mg$\cdot$L^{-1} total Al to pH 8.6 and 0.05 mg$\cdot$L^{-1} total Al (reference pond). In addition to aluminum, concentrations of cadmium, cobalt, iron, manganese, nickel, lead, antimony, arsenic, selenium, zinc, and boron were also elevated in some of the acidic ponds. Contrary to the study by Pajos (1984), high aluminum concentrations in the water were reflected by high aluminum concentrations in above-ground aquatic vegetation. Aluminum concentrations in submerged mosses ranged from less than 100 µg$\cdot$g^{-1} (dry weight) in the reference ponds to more than 4000 µg$\cdot$g^{-1} in aluminum-contaminated ponds. The aluminum content of dead mosses (previous year's growth) was slightly higher than in the current year's growth. Among the vascular plants, Archtophylla fulva and the cotton grass Eriophorum vaginatum had the highest aluminum concentrations in above-ground tissue of 1550 and 950 µg$\cdot$g^{-1} (dry weight), respectively. Aluminum concentrations in Carex were low (<50 µg$\cdot$g^{-1} (dry weight)), irrespective of the aluminum concentrations in the water.

Histochemical staining showed that aluminum in one of the submerged mosses (Leptodictyon riparium) was predominantly found in the cell wall of the fronds (Havas 1985a).

How these plants obtain aluminum is not yet known. Whereas rooted aquatic macrophytes obtain some of their nutrients from sediments (Carignan and Kalff 1980), other nutrients may be taken up directly from the water (Barko 1982). Uptake of nutrients from these two sources varies with species and with water and sediment chemistry. Uptake of aluminum, therefore, is likely to be more complex in aquatic than in terrestrial plants. This is an area which requires further research.

3.3 ALGAE

3.3.1 ALUMINUM CONTENT

A knowledge of aluminum concentrations in algae enables us to determine which species have the ability to accumulate or exclude aluminum, and what the potential is for both biological transport along food chains and biogeochemical cycling. Comparing aluminum concentrations in tolerant and sensitive species may provide some insight regarding the mode of aluminum toxicity as well as detoxification processes. There are few studies that provide aluminum concentrations in algae. In one study (Boyd and Lawrence 1967), aluminum concentrations for six species of freshwater algae ranged from 620 to 4500 µg$\cdot$g^{-1} (dry weight). Microcystis had the lowest concentration and Rhizoclonium the highest (Table 3-4). In marine species, aluminum concentrations range from 7 µg$\cdot$g^{-1} to more than 2800 µg$\cdot$g^{-1} (Martin and Knauer 1973). How comparable these values are is difficult to establish, as the analytical techniques, methods of collection, environmental chemistry, and aluminum concentrations are all highly variable. Whether the aluminum is absorbed or adsorbed cannot be determined from these data.

In a more recent study, Stokes (1985) tested the effect of fulvic acid on the uptake of aluminum by Mougeotia. Mougeotia were exposed for 24 h to 100 µg$\cdot$L^{-1} Al at pH 5.0, with (4.5 mg$\cdot$L^{-1} Ca) and without fulvic acid.

Table 3-4. Aluminum concentrations in algae.

Species	Aluminum ($mg \cdot kg^{-1}$ (dry weight))		Habitat	Comments	Reference
Microcystis	620		Fresh water		Boyd and Lawrence 1967
Euglena	1200		"		
Spirogyra	2800		"		
Chara	2800		"		
Pithophora	4100		"		
Rhizoclonium	4500		"		
Phytoplankton	110	median	Pacific Ocean	No Ti detected	Martin and Knauer 1973
	7-630	range			
	444	median		Ti detected	
	214-2850	range			
	38	median		Sr present	
	11-177	range			
Brown algae	62			CF[α] = 7500	Bowen 1979
Phytoplankton	38-440		Marine	CF = 5000-50 000	
Red algae	1100			Hard parts only	
Halimeda opuntia	260-300 190-220 750		Marine	By X-ray fluorimetric spectrophotometry	Stoklasa 1922 (cited by Bohm 1972)
	120-150 30-40 CF = 2500			Org. water in solution	
Phytoplankton	2500		Fresh water	0.19 $mg \cdot L^{-1}$ in water	Rawlence and Whitton 1977
	3700			0.024 $mg \cdot L^{-1}$	
Phytoplankton	470 average 7-5000 range				Rawlence and Whitton 1977

[α] CF = concentration factor.

She found that fulvic acid altered the total aluminum content of the alga, as well as the partitioning of aluminum by the organism. The bioconcentration factor for aluminum in the treatment without fulvic acid was 35, two-thirds of which was internally bound (based on EDTA rinse), compared with a bioconcentration factor for aluminum in the treatment with fulvic acid of 3, all of which was internally bound. It appears that the ability of algae to take up aluminum from the surrounding medium can be strongly influenced by competing ligands.

In a related study (Stokes *et al*. 1985; see also Havas 1985b), aluminum localization in aluminum-tolerant and aluminum-sensitive strains of *Mougeotia* was compared using hematoxylin (histochemical stain). In the aluminum-sensitive strain, aluminum entered the cell and was associated with the nucleus. In the aluminum-tolerant strain, aluminum appeared to be excluded. To what extent this happens in other species is not known. Perhaps the only point that can be made is that algae are able to concentrate aluminum from the surrounding medium, often to high concentrations. Their ability to do this is species-specific and can be influenced by other chemicals in the surrounding medium.

3.3.2 ALUMINUM TOXICITY

Böhm-Tüchy (1960, cited by Burrows 1977) exposed 17 species of algae to graded concentrations of $Al(NO_3)_3$ for different lengths of time to determine the minimum concentrations of aluminum required to kill algal cells within a defined period. The algal species differed considerably in their tolerance to aluminum. The Desmidiaceae were more tolerant than either *Oedogonium* or members of the Zygnemataceae. The most sensitive species they tested was *Spirogyra varians*, which died within 3 h at 0.135 $mg{\cdot}L^{-1}$ Al. A different species of *Spirogyra* (not identified), isolated from a peat bog, was able to tolerate 200 times higher aluminum concentrations for a similar length of time. The most tolerant species, *Euastrum* sp., survived at 6750 $mg{\cdot}L^{-1}$ for 312 h. (Note that these data are difficult to interpret because no attention was paid to the chemistry of aluminum (notably aluminum-phosphate interactions) in the growth medium.) The results of other experiments (Foy and Gerloff 1972; Becker and Keller 1973; Upitis *et al*. 1975) were similar to those of Böhm-Tüchy (1960, cited by Burrows 1977).

The effect of aluminum on $^{32}P\text{-}PO_4$ uptake and on photosynthetic activity as measured by ^{14}C uptake was studied by Paul (1984) (see also Nalewajko and Paul 1985) in two Ontario lakes. He found that photosynthetic activity (based on ^{14}C uptake) was inhibited by 50% at 0.38 and 0.18 $mg{\cdot}L^{-1}$ Al in St. Nora Lake (pH 6.1-6.6) and Plastic Lake (pH 5.2-6.2), respectively, compared with the control to which no aluminum had been added. Fifty percent $^{32}P\text{-}PO_4$ uptake occurred at even lower aluminum concentrations (0.22 and 0.1 $mg{\cdot}L^{-1}$ Al for St. Nora Lake and Plastic Lake, respectively). At pH 4.5 the effects of aluminum on both ^{32}P and ^{14}C uptake were reduced. In the presence of organic ligands (EDTA or citrate), photosynthetic activity increased slightly, whereas phosphate uptake increased significantly at 0.25 mg·L^{-1} Al. This suggests that the chemical form of the aluminum is critical for photosynthesis and phosphate uptake.

3.3.3 ALGAE IN ACIDIC, ALUMINUM-CONTAMINATED ENVIRONMENTS

It appears that algae are able to tolerate higher concentrations of aluminum than are most freshwater planktonic crustaceans, amphibians, and fish (see Sections 3.4, 3.9, and 3.10). This hypothesis is partially supported by field data. A large number of algal species have been found in aluminum-contaminated waters, and these are listed in Table 3-5. This table is based on species found in acidified lakes and streams; acidic sulfur springs at Yellowstone; acidic, metal-contaminated tundra ponds at the Smoking Hills; acid mine drainage ponds and streams; and organically acidic mires. Most of these environments are devoid of fish and have a restricted invertebrate community.

Of the 168 species of algae listed in Table 3-5, 51% are members of the Chlorophyta, 35% are members of the Chrysophyta, and the remaining species belong to the Cyanophyta (7%), Euglenophyta (3%), Pyrrophyta (2%), and Cryptophyta (1%). Desmids (41 species) and pennate diatoms (53 species) make up 56% of the species found in aluminum-contaminated water. Many of the desmids are restricted to acidic environments high in dissolved organic carbon. Availability of aluminum in these environments may be considerably reduced as a result of aluminum-organic binding.

Several species appear to be ubiquitous in acidic, aluminum-contaminated water. These include: Chlamydomonas acidophila (which is synonymous with C. applanata v. acidophila), several Chlorella spp., Oocystis spp., Ulothrix zonata, Microthamnion strictissium, Mougeotia spp., Zygogonium ericetorum, Eunotia exigua, several Nitzschia, Navicula, and Pinnularia spp., Euglena mutabilis, Lepocinelis ovum, and Cryptomonas spp. Some of these species have been found at extremely high concentrations of aluminum (up to 3000 mg·L^{-1}) and exceptionally low pH (as low as pH 1.5).

It is not clear whether the shifts in species composition, productivity, and biomass that are observed in acidified lakes (Kwiatkowski and Roff 1976; Yan and Stokes 1978) are the result of increased H$^+$ concentrations, elevated concentrations of potentially toxic metals, reduced nutrient availability (PO_4) (Hendrey et al. 1980), or changes in grazing pressure or competition. Most likely a combination of these factors plays a role in the biological changes reported in the literature.

Thus, little can be inferred about the effect of aluminum by itself on algae, except that algae isolated from this type of environment can frequently tolerate high aluminum concentrations in laboratory experiments. Hutchinson et al. (1981) found that Euglena mutabilis isolated from an acidic, metal-contaminated environment could survive and grow in solutions containing 50 mg·L^{-1} Al at pH 3. A persistent yeast contaminant,

Table 3-5. Algae found in acidic, aluminum-contaminated water.

Species	Habitat$^{\alpha}$ L	S	SS	SH	AM	O	pH	Aluminum (mg·L^{-1})	Reference$^{\beta}$
CHLOROPHYTA CHLOROPHYCEAE VOLVOCALES									
Chlamydomonas acidophila				X	X		1.8-2.8	18-810	11, 12
C. applanata v. *acidophila*					X		1.8-3	5.8-1570	4
C. polypyrenoideum					X		3-4	ns$^{\gamma}$	8, 15
Chlamydomonas sp.			X		X		2-4	2-411	4, 8, 9, 14
TETRASPORALES									
Radiosphaera minuta					X		ns	ns	11
CHLOROCOCCALES									
Ankistrodesmus convolutus v. *minutus*	X						4	ns	1
A. falcatus					X		≤4	≥2	14
Characium sp.					X		1.5-3	5.8-2500	4
Chlorella protothecoides					X		ns	ns	11
C. saccharophila					X		ns	ns	11
C. saccharophila v. *ellipsoidea*					X		ns	ns	11
C. vulgaris v. *aultophica*					X		ns	ns	11
Closteriopsis longissima					X		≤4	≥2	14
Cylindrocapsa geminella v. *minor*					X		≤4	≥2	14
Gleococcus mucosus						X	3.9-4.1	ns	2
PYRRHOPHYTA									
Gymnodinium sp.	X						4	ns	1
Peridinium cinctum						X	3.8	ns	2
P. inconspicuum	X						4	ns	1
CYANOPHYTA									
Anabaena sp.						X	3.4-4	ns	2
Aphanizomenon flos-aquae					X		3-4	ns	8, 15
Chroococcus minutus						X	3.4-4.1	ns	2
C. turgidus						X	3.4-4.2	ns	2
Hapalosiphon sp.						X	3.4-4.1	ns	2
Merismopedium glauca						X	3.5-4.1	ns	2
Nostoc paludosum						X	3.6	ns	2
Nostoc sp.						X	3.7	ns	2

Table 3-5. (Cont'd)

Species	Habitat						pH	Aluminum $(mg\cdot L^{-1})$	Reference
	L	S	SS	SH	AM	O			
CYANOPHYTA (Cont'd)									
Oscillatoria sp.				X	X		≤4-8.2	≤0.3-≥2	12, 14
Porphyrosiphon notarissii					X		≤4	≥2	14
Scytonema sp.						X	4.0	ns	2
Stigonema sp.						X	4.0-4.2	ns	2
Rhoicosphenia curvata					X		≤3	≥2	6, 14
Stauroneis anceps					X		≤4	≥2	14
Stephanodiscus hantzschii					X		≤4	≥2	14
Surirella biseriata					X		ns	ns	6
S. ovalis					X		≤4	≥2	6, 14
S. saxonica					X		ns	ns	6
Synedra acus				X	X		≤4-8.2	≤0.3-≥3	12, 14
S. ulna					X		ns	ns	6
Tabellaria fenestrata						X	3.9-4.1	ns	2
T. floculosa		X			X		≤4	≥3	14
EUGLENOPHYTA									
Euglena mutabilis				X	X		1.5-4	2-3130	4, 6, 8, 12, 14
Euglena sp.			X	X		X	3.4-8.2	≤0.6	2, 9, 12
Lepocinclis ovum					X		2.5-4	72-400	4, 8
Petalomonas polytaphrena						X	3.8-4.0	ns	2
Trachelomonas sp.					X		≤4	≥2	14
CRYPTOPHYTA									
Cryptomonas ovata				X			3.6-8.1	≤0.3-3.8	12
Cryptomonas sp.				X	X		1.8-8.2	≤0.3-600	4, 12, 14
Gomphonema sp.					X		≤4	≥2	14
Melosira granulata					X		≤4	≥2	14
Meridion lanceolata					X		≤4	≥2	6, 14
Navicula lanceolata				X	X		≤8.2	≤0.3	6, 12
N. mutica v. *intermedia*					X		ns	ns	11
N. nivalis					X		2.5	4.7	4
N. oblonga					X		ns	ns	6
N. subtilissima						X	3.6-3.8	ns	2
N. tuscula				X			3.6-8.2	≤0.3-3.8	12
N. viridis					X		ns	ns	6
Navicula sp.				X	X		2.5-8.2	≤0.3-4.9	4, 8, 12, 14
Nitzschia confinis					X		ns	ns	11
N. communis				X			1.8-3.6	3-800	12
N. elliptica v. *alexandria*					X		2.5-3	4.8-411	4
N. hungarica					X		≤4	≥2	14
N. ovalis					X		2.5-2.8	4.9-82	4
N. palea				X	X		1.8-3	4-39	4, 12
N. parvuloides					X		ns	ns	11

Table 3-5. (Cont'd)

Species	Habitat						pH	Aluminum (mg·L^{-1})	Reference
	L	S	SS	SH	AM	O			
CRYPTOPHYTA (Cont'd)									
N. sigmoidea					X		ns	ns	6
N. subcapitellata					X		2.5-3	3.7-325	4
Nitzschia sp.				X			2.5-8.2	≤0.3-411	4, 12
Pinnularia acoricola					X		1.5-3	3-2500	4
P. biceps v. *petersonii*					X		ns	ns	11
P. hilseana v. *hilseana*					X		≤4	≥2	14
P. microstauron					X		2.5-2.9	3.7-4.9	4, 11
P. molaris				X			2.8	18	12
P. obscura					X		ns	ns	12
P. termitina					X		≤4	≥2	14
P. viridus					X		ns	ns	11
CHRYSOPHYTA CHRYSOPHYCEAE									
Chromulina sp.					X		2-8.2	≤0.3	8, 12
Dinobryon sp.		X					4	ns	5
Ochromonas sp.					X		≤4	≥2	14
Phaeothamnion sp.					X		2-3	ns	8
BACILLARIOPHYCEAE CENTRALES									
Cyclotella glomerata					X		≤4	≥2	8
Melosira granulata					X		≤4	≥2	8
PENNALES									
Achnanthes marginula					X		≤4	≥2	8
Asterionella formosa						X	4.1	ns	2
Cocconeis diminuta					X		≤4	≥3	14
C. pediculus					X		ns	ns	6
C. placentula				X	X		≤8.2	≤0.3	6, 12
Cocconeis spp.					X		ns	ns	6
Denticula spp.					X		ns	ns	6
Eunotia arcus				X			2.8-3.6	3-20	12
E. exigua					X	X	2.5-4	2-212	2, 4, 11, 13, 14
E. glacialis				X			1.8-3.6	3-800	12
E. lunaris		X					4	ns	5
Fragilaria sp.					X		≤4	≥2	14
Frustulia rhomboides v. *saxonica*					X		≤4	≥2	14

Table 3-5. (Cont'd)

Species	Habitat L	S	SS	SH	AM	O	pH	Aluminum $(\mathrm{mg \cdot L^{-1}})$	Reference
PENNALES (Cont'd)									
F. saxonica						X	4.0-4.1	ns	2
Netrium digitus						X	3.6-4.1	ns	2
N. oblongum						X	3.6-4.1	ns	2
Penium polymorphum						X	4	ns	2
P. silvae-nigrae						X	3.7	ns	2
P. silvae-nigrae v. parallelum						X	3.4-4.0	ns	2
Pleurotaenium minutum						X	3.7-4.2	ns	2
P. trabecula						X	3.6-3.8	ns	2
P. tridentulum						X	3.8-3.9	ns	2
Spirogyra sp.					X	X	≤4.1	≥2	2, 14
Staurastrum alternans					X		≤4	≥2	14
S. elongatum						X	3.4-4.2	ns	2
S. hystrix						X	3.8-4.1	ns	2
S. orbiculare						X	3.8	ns	2
S. paradoxum						X	4.1	ns	2
S. polymorphum						X	3.8-4.1	ns	2
S. quadrispinatum						X	3.4-4.2	ns	2
S. sexangulare						X	4.1-4.2	ns	2
S. tohopekaligense						X	3.8-4.0	ns	2
Staurodesmus extensus						X	3.8	ns	2
S. megacanthus						X	4.1	ns	2
S. sellatus						X	3.8	ns	2
Xanthidium antilopaeum						X	3.6-4.1	ns	2
X. antilopaem v. laeve						X	3.8-4.1	ns	2
Zygogonium ericetorum		X			X	X	2.4-4.1	2-411	2, 4, 9, 14
ZYGNEMATALES									
Actinotaenium cucurbita						X	3.4-4.2	ns	2
A. cucurbitinum						X	3.8	ns	2
Ankistrodesmes convolutus v. minitus	X						4	ns	1
A. falcatus					X		≤4	≥2	14
Bambusina Borreri						X	3.4-4.1	ns	2
Closterium acerosum					X		≤4	≥2	14
C. longissima					X		≤4	ns	14
C. ulna						X	4.1	ns	2
Closterium sp.					X		3-4	ns	15
Cosmarium granatum				X			3.6, 3.8	4	12
C. moniliforme						X	4.1	ns	2
C. pygmaeum						X	3.7-4.1	ns	2
C. rectangulare						X	4.0-4.2	ns	2
C. taxichondriforme						X	3.8-4.1	ns	2
C. turpinii						X	4.1	ns	2
Cosmarium sp.				X	X		2.8-8.2	≤0.3-18	12, 14

Table 3-5. (Cont'd)

Species	Habitat L	S	SS	SH	AM	O	pH	Aluminum (mg·L^{-1})	Reference
ZYGNEMATALES (Cont'd)									
Cylindrocapsa geminella v. *minor*					X		≤4	≥2	14
Cylindrocystis brebissonii						X	3.6-4.1	ns	2
Desmidium sp.					X		3-4	ns	8
Euastrum insulare						X	3.8-4.1	ns	2
E. montanum						X	3.8	ns	2
Gonatozygon monotaenium						X	4.2	ns	2
Micrasterias arcuata						X	3.8-4.2	ns	2
M. crux-melitensis						X	4.0-4.2	ns	2
M. truncata						X	4.1	ns	2
Mougeotia scalaris	X						4	ns	1
Mougeotia sp.	X	X			X	X	2-8.2	≤0.3	2, 3, 5, 8, 10, 12
Oocystis lacustris	X						4	ns	1
O. solitaria						X	3.6-4.2	ns	2
O. solitaria v. *major*				X			3.6-8.1	≤0.3-3.8	12
O. submarina	X			X			4-8.1	0.3	
Oocystis sp.					X		≤4	≥2	14
Scenedesmus abundans					X		≤4	≥2	14
ULOTRICHALES									
Binuclearia tetrana	X				X		≤4	≥2	5, 14
Hormidium rivulare					X		2.5-3	4.8-411	4
Microspora pachyderma					X		≤4	≥2	14
Stichococcus bacillaris					X		1.8-2.8	32-890	4, 11
Ulothrix subtilissima					X		ns	ns	11
U. tenerrima					X		≤4	≥2	7, 14
U. variabilis					X		ns	ns	11
U. zonata					X		2-3	138	4, 8
OEDOGONIALES									
Bulbochaete sp.						X	4	ns	2
Oedogonium sp.						X	3.4-4.2	ns	2
CHAETOPHORALES									
Microthamnion strictissium					X		2.9-4	2-169	4, 14
Ochromonas sp.					X		≤4	≥2	14
Protococcus viridis					X		≤4	≥2	14
Stigeoclonium subtile					X		≤4	≥2	14

Table 3-5. (Cont'd)

[α] Abbreviations used:

L = lake
S = stream
SS = sulfur spring
SH = Smoking Hills ponds
AM = acid mine water
O = organic-rich waters.

[β] References:
1. Almer *et al*. 1974
2. Flensburg and Sparling 1973
3. Grahn *et al*. 1974
4. Hargreaves *et al*. 1975
5. Hendrey 1982
6. Joseph 1953
7. Koryak *et al*. 1972
8. Lackey 1938
9. Lynn and Brock 1969
10. Nilssen 1980
11. Richards 1973 (cited by Riley 1977)
12. Sheath *et al*. 1982
13. Van Dam *et al*. 1980
14. Warner 1971
15. Campbell *et al*. 1964

[γ] ns = not specified.

Crytococcus sp., always occurred with Euglena mutabilis in the field. When the yeast was deliberately added to the cultures, the growth of both the yeast and the algae improved markedly. Growth of the Euglena in all treatments (pH 1-8, 0-50 $mg{\cdot}L^{-1}$ Al) was enhanced by the yeast. The exact nature of this mutualism is not known, although it has been hypothesized that the Euglena provides the yeast with an organic carbon source while the metabolic excretions from the yeast may augment the nitrogen and possibly inorganic carbon requirements of the alga, as well as produce organic ligands which bind aluminum and other metals (Hutchinson et al. 1981).

In higher plants that are aluminum-sensitive, aluminum seems to interfere with calcium uptake and transport. When Chlorella pyrenoidosa (a green alga with no measurable calcium requirement) was tested, the results showed that it had a fairly high aluminum tolerance (Foy and Gerloff 1972). Most of the cells died at 12 and 24 $mg{\cdot}L^{-1}$ Al, but were actually stimulated by 3 and 6 $mg{\cdot}L^{-1}$ compared with the control (0 $mg{\cdot}L^{-1}$). Unfortunately, a considerable amount of ferric citrate, citric acid, and P was used in the culture medium, and these may have complexed the aluminum and thus reduced its availability. Also the pH of the culture solutions was not maintained during the experiment, and increased rapidly from 4.6 to 7.8 as a result of photosynthetic activity. This increase in pH could have detoxified the aluminum in the culture solutions. Experiments that were initiated at a higher pH (pH 8-9) showed reduced aluminum toxicity.

Work with Scenedesmus quadricauda, which has a measurable calcium requirement, indicated that its 28-h toxicity threshold was between 1.5 and 2.0 $mg{\cdot}L^{-1}$ Al (Bringmann and Kuhn 1959, cited by Burrows 1977). Whether this apparent difference in sensitivity between the algal species was real or was the result of differences in aluminum speciation cannot be evaluated.

A different species of Chlorella (C. vulgaris) grew best at 8.7 $mg{\cdot}L^{-1}$ Al (Bertrand and de Wolf 1966, cited by Burrows 1977). After 4 weeks at 317 $mg{\cdot}L^{-1}$, growth was reduced by 50% (Becker and Keller 1973, cited by Burrows 1977). Once again, because aluminum speciation is critical for determining aluminum toxicity, it is difficult to compare these results.

In order to do a comparative study, it is necessary to culture different species in the same medium at comparable pH levels. Because dense populations of algae in batch cultures alter the pH of the solutions, a flow-through system using lower cell density may be required to determine aluminum toxicity. Extracellular products can have a profound effect on aluminum chemistry and should also be considered in dense cultures.

3.3.4 INDUCING ALUMINUM TOLERANCE

Perhaps one of the most interesting results obtained by Foy and Gerloff (1972) indicated that aluminum tolerance can be induced and/or selected for within a few generations by subjecting cells to increased aluminum stress. Their "tolerant" strain was able to survive and grow slowly at 48 mg•L^{-1} Al and pH 4.2, whereas their less tolerant strain died at 12 mg•L^{-1}. It was suggested that aluminum readily penetrates plants with poorly developed plasmalemmas, rendering the outer layers of the protoplasm less subject to plasmolysis as a result of solidification. Plants with a well-developed plasmalemma are able to tolerate higher concentrations of aluminum and appear to be better protected from metal ions.

3.3.5 ALUMINUM AS AN ESSENTIAL MICRONUTRIENT

Three species of Chlorella (C. pyrenoidosa, C. saccharophila, and C. vulgaris) for which aluminum toxicity data are available are all stimulated in the presence of aluminum. Maximum growth occurred at 6 and 12 mg•L^{-1} for nonselected and selected strains of C. pyrenoidosa, respectively; at 1 and 10 mg•L^{-1} for C. saccharophila at pH 5 and 3, respectively; and at 8.7 mg•L^{-1} for C. vulgaris. Aluminum may be an essential micronutrient for these species. However, once again it must be remembered that high concentrations of citric acid and phosphorus in the culture medium and lack of pH control during the experiment make it difficult to determine how much of the aluminum in the culture solution was available for uptake by the algae.

Acid-washed diatoms readily accumulate aluminum (Martin and Knauer 1973). This is probably also true for non-acid-washed diatoms, as the aluminum content of diatomaceous earth is quite high. In marine plankton, aluminum levels range from 27 to 52% in the silicon fraction (Martin and Knauer 1973). Diatoms are common in aluminum-contaminated environments, and it has been suggested that aluminum reduces the solubility of diatom frustules by forming relatively insoluble aluminosilicate. Nitzschia communis, isolated from an acidic pond (pH 1.8, more than 500 mg•L^{-1} Al in the water), had a thickened frustule (Sheath et al. 1982). Whether this thickening was because of the elevated aluminum in the water and whether this affected its ability to survive are not known.

3.4 MICROCRUSTACEANS

3.4.1 DISTRIBUTION

In a recent study, Bleiwas (1983) examined the distribution of zooplankton in six Ontario lakes that ranged from pH 7.1 to 4.6 and from 0.032 to 0.49 mg•L^{-1} Al. Even in the most acidic, aluminum-contaminated lake (Ruth-Roy), Diaptomus minutus, Holopedium gibberum, Diaphanosoma birgei, Eubosmina tubicens, Bosmina longirostris, Alona sp., and Chydoridae were found. The first two species were the most abundant in this lake. Other studies (Almer et al. 1974; Sprules 1975; Roff and Kwiatkowski 1977; MOE 1982a,b; Confer et al. 1983) also report an increase in the dominance of H. gibberum, B. longirostris, and D. minutus in acidic lakes. Additional species that can survive at concentrations of aluminum in excess of 0.1 mg•L^{-1} and below pH 5.6 include Daphnia ambigua, D. catawba, D. retrocurva, Eurycercus sp., Leptodora kindtii, Polyphemus pediculus, Diaptomus oregonensis, D. reinhardi, Cyclops bicuspidatus thomasi, Mesocyclops edax, and Tropocyclops prasinus (Bleiwas 1983).

If we assume that species in acidic lakes (<pH 5.5) are at least potentially aluminum-tolerant, then the list of potentially aluminum-tolerant crustaceans may include those in Table 3-6. Interestingly, despite the fact that daphnids are noted for their sensitivity to low pH, seven species were found below pH 4.6. Some of these daphnids survived aluminum concentrations in excess of 1.0 $mg \cdot L^{-1}$.

3.4.2 MORTALITY AND REPRODUCTION

Perhaps the most frequently studied crustacean is the water flea, Daphnia magna. One of the earlier studies concerned with the effect of aluminum on D. magna was conducted by Anderson (1948). He found that aluminum in excess of 1.35 $mg \cdot L^{-1}$ was toxic when added as $AlCl_3$ to Lake Erie water at pH 8.2. Toxicity was defined by Anderson as the concentration that resulted in immobilization of Daphnia within 64 h.

Biesinger and Christensen (1972) also examined the effect of aluminum on D. magna and found that the acute 48-h LC_{50}, without food, occurred at 3.9 $mg \cdot L^{-1}$ Al, whereas the chronic 3-week LC_{50} occurred at 1.4 $mg \cdot L^{-1}$ Al. Considerably lower concentrations of aluminum affected reproduction. Fifty and 16% reproductive impairment were observed at 0.68 and 0.32 $mg \cdot L^{-1}$ Al, respectively, in Lake Superior water (pH 7.4-8.2; alkalinity 41-50 $mg \cdot L^{-1}$; 14 $mg \cdot L^{-1}$ Ca; 1 $mg \cdot L^{-1}$ Na; 0.001-0.02 $mg \cdot L^{-1}$ Al).

Based on the results of Anderson (1948) and Biesinger and Christensen (1972), D. magna appears to be able to tolerate relatively high levels of aluminum, much higher than those that normally occur in even moderately acidic lakes. However, it is known that the toxicity of aluminum, at least to fishes and freshwater plants, is influenced by the amount of Ca and H ions in the water (Foy et al. 1979; Brown 1983). In neither of these experiments was the pH monitored. Anderson stated that the pH decreased in the water to which aluminum was added, but he was not specific. Also, the calcium concentrations are higher in both Lake Superior and Lake Erie than in those lakes that are sensitive to acidification. These two factors, therefore, could significantly alter aluminum toxicity to D. magna.

In a more recent study, Havas (1985a) examined the effect of aluminum on D. magna. In this study, the toxicity of aluminum was determined at different pH levels (pH 6.5, 5.0, 4.5) and at two calcium concentrations (2.5, 12.5 $mg \cdot L^{-1}$ Ca). Water from a circumneutral, soft-water lake in New Hampshire (Mirror Lake: pH 6.6, 2.45 $mg \cdot L^{-1}$ Ca, 1.76 $mg \cdot L^{-1}$ Na, ≤ 0.02 $mg \cdot L^{-1}$ Al) was used in this study. The results clearly showed that the toxicity of aluminum to D. magna varied with both pH and the concentration of calcium. Maximum aluminum toxicity occurred at pH 6.5 (Figure 3-1). Interestingly, at lower pH levels (pH 4.5), aluminum

Table 3-6. Minimum pH and maximum aluminum concentrations at which crustaceans have been recorded in North America.

Species	Minimum pH	Maximum Al concentration (µg·L⁻¹)	References[α]
CLADOCERA			
Acantholeberis curvirostris	4.1	381	6
Alona affinis	4.1	381	6
A. quadrangularis	4.7	?	3
A. rectangula	4.7	?	3
Alona sp.	4.6	490	4
Bosmina coregoni	4.7	?	1
B. longirostris	4.1	1097	2, 3, 4, 5, 6
Ceriodaphnia megalops	4.1	1097	6
Chydorus sphaericus	4.1	1097	3, 6
Chydoridae	4.6	490	4
Daphnia ambigua	4.3	1097	1, 3, 4, 6
D. catawba	4.2	150	1, 2, 3, 4, 5
D. galeata mendotae	4.05	1097	1, 2, 5, 6
D. longiremis	4.45	87	2, 5, 6
D. parvula	4.6	?	1
D. pulicaria	4.2	?	1
D. retrocurva	4.05	1097	1, 2, 4, 5, 6
Diaphanosoma birgei[β]	4.2	490	4
D. leuchtenbergianum	4.05	1097	1, 2, 3, 5, 6
Eubosmina tubicens	4.05	490	4, 5
Eubosmina spp.	4.1	381	7
Holopedium gibberum	4.05	490	1, 2, 3, 4, 5
Latona setifera	4.6	381	6
Leptodora kindtii	4.55	150	1, 2, 4, 5
Macrothrix laticornis	4.1	381	6
Ophroyoxus gracilis	4.05	440	5, 6
Polyphemus pediculus	4.05	490	1, 3, 4, 5, 6
Simocephalus serrulatus	4.1	1097	6
S. vetulus	4.6	440	7
CALANOID COPEPODS			
Diaptomus minutus	3.8	490	1, 2, 3, 4, 5, 6
D. oregonensis	4.29	1097	2, 6
D. spatulocrenatus	4.7	?	3
Epischura lacustris	4.1	1097	2, 3, 6
Senecella calanoides	4.4	?	6
CYCLOPOID COPEPODS			
Cyclops bicuspidatus thomasi	4.05	1097	1, 2, 4, 5, 6
C. scutifer	4.6	440	2, 3, 7
C. vernalis	4.1	1097	6, 7
Cyclops sp.	2.8	18000	8
Eucyclops agilis	4.29	1097	3, 6
Eucylcops sp.			
Mesocyclops edax	4.05	150	1, 2, 3, 4, 5
Orthocyclops modestus	4.29	1097	1, 6
Tropocyclops prasinus mexicanus	4.29	1097	1, 2, 3, 6

[α] References:
1. Sprules 1975
2. Keller and Conroy 1981
3. Confer *et al*. 1983
4. Bleiwas 1983
5. Roff and Kwiatkowski 1977
6. Ministry of the Environment 1982a, b
7. Yan *et al*. 1982
8. Havas and Hutchinson 1983

[β] Identified as *D. leuchtenbergianum* in earlier studies.

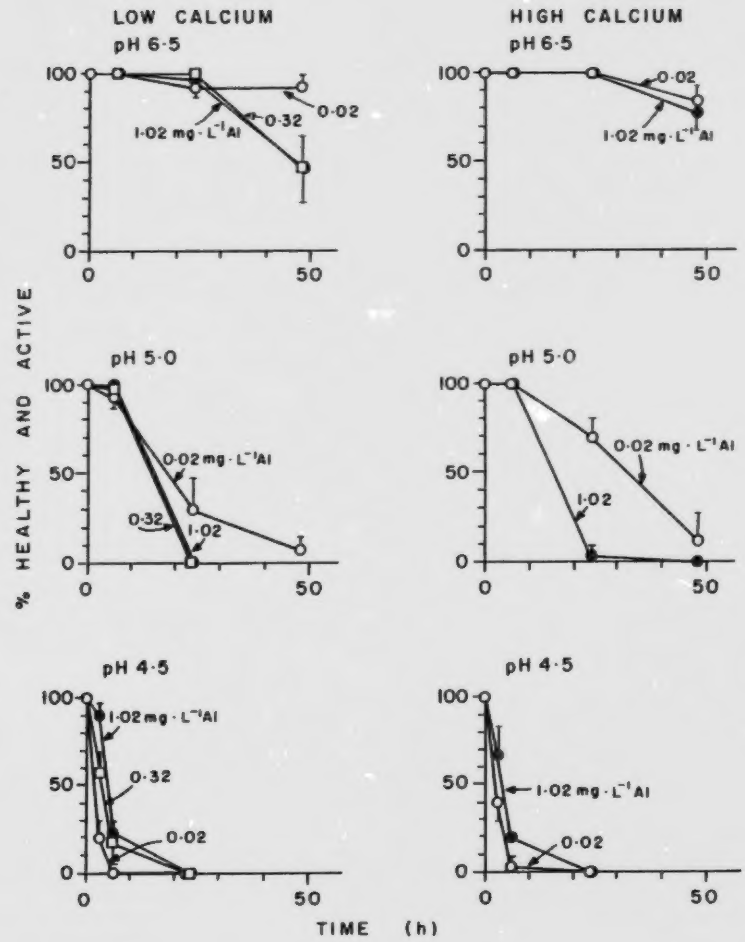


Figure 3-1. Survival of Daphnia magna exposed to low pH (pH 6.5, 5.0, 4.5) and elevated concentrations of aluminum (0.02 (reference treatment), 0.32, 1.02 $mg \cdot L^{-1}$) in water containing 2.5 $mg \cdot L^{-1}$ Ca (low Ca) and 12.5 $mg \cdot L^{-1}$ Ca (high Ca). Bars represent one standard deviation of three replicates (from Havas 1985a).

temporarily reduced H^+ toxicity. Calcium also reduced aluminum toxicity, but only at pH 6.5 (Figure 3-1). Based on this study, 0.32 $mg \cdot L^{-1}$ Al appears to be toxic to *D. magna* in soft water at circumneutral pH. Aluminum concentrations of this magnitude have been reported for moderately acidic lakes. Based on the work by Biesinger and Christensen (1972), significantly lower concentrations of aluminum are likely to affect reproduction and chronic toxicity. It appears, therefore, that *D. magna* is quite sensitive to aluminum in lakes that have low calcium concentrations and pH levels that are not intrinsically toxic.

Experiments have also been conducted with species that commonly occur in acidified lakes (i.e., *Daphnia catawba* and *Holopedium gibberum*) (Havas and Likens 1985a). Both of these species were collected from and tested in Mirror Lake water. They were considerably more tolerant of aluminum than was *D. magna*. Maximum aluminum toxicity occurred at pH 6.5 and 5.0 for both crustaceans. Based on this study, it is likely that *D. catawba* and *H. gibberum* will be able to survive in acidified lakes even if concentrations of aluminum continue to increase as a result of continued acidification.

It is interesting that for the three species, *D. magna*, *D. catawba*, and *Holopedium gibberum*, maximum aluminum toxicity occurred between pH 5 and 6.5. Results for three fish species were similar. Baker (1981) reported maximum aluminum toxicity between pH 5.0 and 5.5 for brook trout (*Salvelinus fontinalis*) and white sucker (*Catostomus commersoni*), whereas Muniz and Leivestad (1980b) observed maximum toxicity to brown trout (*Salmo trutta*) at pH 5.1 and 5.5. Therefore, it is possible that the mode of aluminum toxicity is similar for both crustaceans and fish.

It is difficult to separate the effects of aluminum and other metals from those of H^+ under natural conditions. In one study, Havas and Hutchinson (1982) exposed four species of crustaceans (*Daphnia middendorffiana*, *Diaptomus arcticus*, *Branchinecta paludsoa*, *Lepidurus arcticus*) to metal-contaminated pond water containing 20 $mg \cdot L^{-1}$ Al, and to uncontaminated or "reference" water adjusted to different pH levels. They found that the mortality of all four species was greater at pH 4.5 and 5.5 in the metal-contaminated water than in the reference water. Additional experiments revealed that of the six elements tested (Ca, Na, Al, Fe, Ni, Zn), only the difference in aluminum concentrations could account for the additional toxicity of the metal-contaminated water.

3.4.3 ALUMINUM CONTENT

In a recent study, Havas (1985a) found that aluminum is rapidly taken up by *Daphnia magna*. In one experiment, daphnids were exposed to 1.02 $mg \cdot L^{-1}$ Al at pH 6.5 for 24 h. Concentrations of aluminum in/on these daphnids increased from 350 to 11 200 $\mu g \cdot g^{-1}$ (Table 3-7). Even at more realistic values of 0.32 $mg \cdot L^{-1}$ Al in the water and pH 5.0, the concentration of aluminum in the *Daphnia* increased from 189 to 1670 $\mu g \cdot g^{-1}$.

Table 3-7. Aluminum content of *Daphnia magna* at different pH levels and external aluminum concentrations[α] (from Havas 1985a).

		Aluminum concentration in the water (mg·L^{-1})		
pH	Units	0.02[β]	0.32	1.02
6.5	mmol·L^{-1} (μg·g^{-1})	13 ± 3 (351 ± 81)	114 ± 69 (3080 ± 69)	415 ± 170 (11 200 ± 4590)
5.0	mmol L^{-1} (μg·g^{-1})	7 ± 6 (189 ± 162)	62 ± 33 (1670 ± 890)	113 ± 16 (3050 ± 432)
4.5	mmol·L^{-1} (μg·g^{-1})	3 ± 1 (81 ± 27)	17 ± 4 (459 ± 108)	61 ± 10 (1650 ± 270)

[α] Means and standard deviations of three replicate samples are provided in mmol·L^{-1} and in μg·g^{-1}.

[β] Background aluminum concentration in the water was 0.02 ± 0.01 mg·L^{-1} (7.4 x 10^{-4} mmol·L^{-1}).

Although pH had a significant effect on aluminum uptake, calcium concentrations in the water did not.

In crustaceans, such as Daphnia, Holopedium, and Branchinecta, aluminum appeared to be associated with chloride cells, which function as organs for salt uptake as do gills in fish (Havas 1985b). Aluminum may also be adsorbed to the carapace or found in the hind gut as a result of anal drinking (Havas 1985b).

Aluminum concentrations vary considerably in different species. Creed (1984; Appendix III.0) examined the chemical composition of zooplankton collected from 12 lakes in south-central Ontario. These lakes had fall pH levels ranging from 6.01 to 8.72 and aluminum concentrations from 0.09 to 0.37 $mg \cdot L^{-1}$. The zooplankton were separated into three groups, Holopedium gibberum, Daphnia spp., and copepods. Concentrations of aluminum in Daphnia spp. varied from 300 $\mu g \cdot g^{-1}$ in Bass Lake (0.09 $mg \cdot L^{-1}$ Al, pH 8.72) to 9400 $\mu g \cdot g^{-1}$ in Nelson Lake (0.25 $mg \cdot L^{-1}$ Al, pH 6.96). Aluminum concentrations ranged from 700 $\mu g \cdot g^{-1}$ (Plastic Lake, 0.37 $mg \cdot L^{-1}$ Al, pH 6.09) to 14 000 $\mu g \cdot g^{-1}$ (Joe Lake, 0.23 $mg \cdot L^{-1}$ Al, pH 6.42) in Holopedium, and from 90 $\mu g \cdot g^{-1}$ (McFarlane Lake, 0.30 $mg \cdot L^{-1}$ Al, pH 7.81) to 49 000 $\mu g \cdot g^{-1}$ (Horseshoe Lake, 0.03 $mg \cdot L^{-1}$ Al, pH 7.07) among the copepods. There were no significant correlations between aluminum concentrations in the water and those in the biota. The highest aluminum concentrations in the biota were observed between pH 6.4 and 7.1, and decreased at both higher and lower pH levels.

3.4.4 PHYSIOLOGICAL RESPONSES

Although the physiological mechanisms of aluminum toxicity are incompletely understood, it appears that aluminum, like H^+, may interfere with salt balance in aquatic animals. Havas (1985a) examined the effect of aluminum on mortality, and on sodium, chloride, and calcium contents of Daphnia magna. Mortality of the daphnids in the presence of aluminum (at or above 0.32 $mg \cdot L^{-1}$) and also at low pH (at or below pH 5.0) was associated with a net loss of Na and Cl but not of Ca. Only at pH 5.0 with equimolar concentrations of aluminum and calcium in the water was there a decrease in total body calcium content, which was negatively correlated with aluminum content (Figure 3-2).

Although aluminum and hydrogen ions both interfere with sodium regulation, it is possible to distinguish between these effects using ^{22}Na. Experiments (Havas and Likens 1985b) showed that aluminum inhibited ^{22}Na uptake at pH 6.5 and 5.0, but had no additional effect to that of H^+ at pH 4.5. Aluminum increased ^{22}Na outflux at pH 6.5, had no additional effect to that of H^+ at pH 5.0, and temporarily decreased ^{22}Na outflux at pH 4.5. These data suggest that aluminum has two distinct effects on sodium regulation in D. magna. One effect is that aluminum inhibits uptake; it could denature the enzyme ATPase, which is responsible for the active uptake of sodium, or it could interfere with calmodulin, which stimulates ATPases.

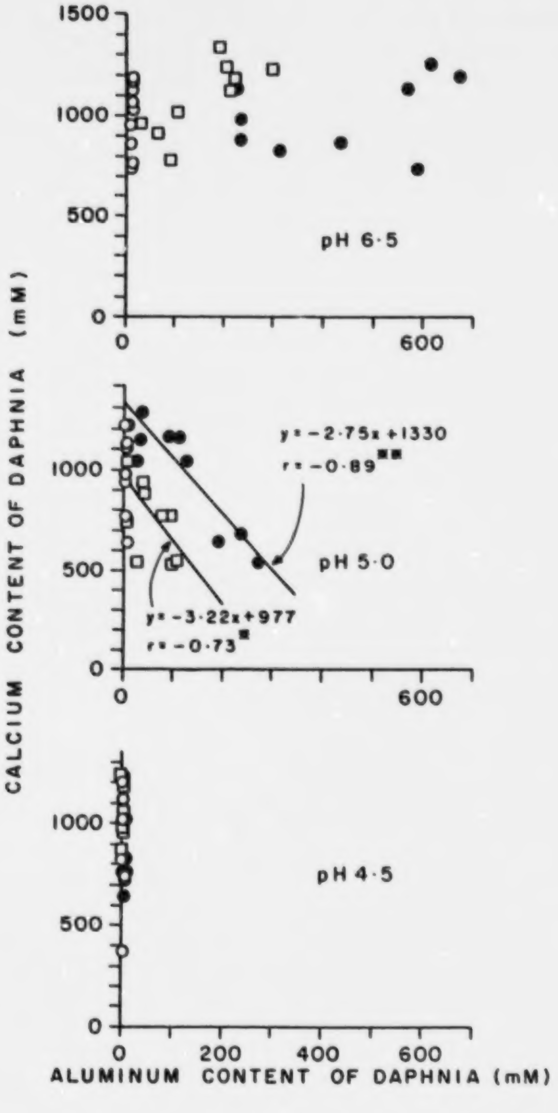


Figure 3-2. Calcium and aluminum contents of Daphnia magna as a function of pH and aluminum concentrations in the water. Each point represents the average of 20 adult daphnids (* = $P \leq 0.05$; ** = $P \leq 0.01$). o = 0.02 mg·L^{-1} Al; □ = 0.32 mg·L^{-1} Al; ● = 1.02 mg·L^{-1} Al (from Havas 1985a).

The other effect is on sodium loss, which may be a result of either increased membrane permeability or increased ion losses through the kidney.

3.5 CRAYFISH

Crayfish have been reported in slightly acidic lakes in Ontario (Collins *et al*. 1981), although they are considered to be moderately sensitive and scarce below pH 5.5 (Malley 1980). Maximum sensitivity occurs during postmolt, and appears to be the result of problems with calcium uptake.

Malley and Chang (1985) examined the effect of aluminum on active uptake of calcium by the gills of the crayfish, *Orconectes virilis*. They found that both aluminum and hydrogen ions inhibited the active uptake of ^{45}Ca by crayfish during postmolt. ^{45}Ca uptake at pH 5.5 was inhibited primarily by the low pH (70%) and only partly by aluminum (10%). Aluminum did not affect calcium uptake at higher pH levels (pH 6.0-6.7) or at lower pH (below pH 5.0). There was no dose-response relationship between aluminum concentration (0.2-1.0 mg·L^{-1}) and calcium uptake at pH 5.5, which may be because of the relatively low aluminum solubility (0.01-0.05 mg·L^{-1}) at this pH.

3.6 INSECTS

3.6.1 DISTRIBUTION

There are several species of insects which occur in extremely acidic, metal-contaminated environments. Some of these appear to be able to survive and reproduce below pH 3.0 and above 10 mg·L^{-1} Al (Table 3-8), conditions that would kill fishes, crustaceans, and most rotifers within minutes. Dytiscid beetles (Coleoptera), blackfly larvae (Megaloptera), chironomid and *Chaoborus* larvae (Diptera), as well as the occasional caddisfly (Trichoptera) and stonefly (Plecoptera) are found in these extreme environments. Oligochaetes and tubificids have also been reported (Parsons 1968; Warner 1971; Havas 1980), whereas mayflies (Ephemeroptera) are conspicuously absent or rare.

3.6.2 ALUMINUM TOXICITY

The effects of aluminum at different pH levels on mortality of *Chaoborus punctipennis* and *Chironomus anthrocinus* larvae were examined (Havas and Likens 1985a). Both of these species were extremely acid-tolerant and were able to survive even at 1.02 mg·L^{-1} Al, despite the fact that they were collected from a circumneutral soft-water lake, which had only 0.02 mg·L^{-1} Al. Experiments with *C. riparius* (which is closely related to *C. anthrocinus*) from the Smoking Hills showed that it could survive aluminum concentrations in excess of 20 mg·L^{-1} (Havas and Hutchinson

Table 3-8. Minimum pH and maximum aluminum concentrations at which insects have been recorded in North America.

Species	Minimum pH	Maximum Al concentration (mg·L^{-1})	References
OLIGOCHAETA			
Tubificidae			
Rhyacodrilus montana	4.05	-	Roff and Kwiatkowski 1977
Lumbriculidae			
Stylodrilus heringianus	4.05	-	Roff and Kwiatkowski 1977
COLEOPTERA			
Dytiscidae			
Oreodytes	4.05	-	Roff and Kwiatkowski 1977
LEPIDOPTERA			
Synclita sp.	3.3	11	Warner 1971
ODONATA			
Ophiogomphus sp.	-	-	Parsons 1968
Pantala hymenea	-	-	Parsons 1968
TRICHOPTERA			
Chematopsyche	-	-	Parsons 1968
Phylocentropus sp.	4.05	-	Roff and Kwiatkowski 1977
Psychomyiid	4.05	-	Roff and Kwiatkowski 1977
Pycnopsyche sp.	2.8	33	Warner 1971
Rhyacophyla sp.	3.8	6	Warner 1971
PLECOPTERA			
Brachyptera sp.	3.8	6	Warner 1971
Nemoura sp.	3.5	8	Warner 1971
MEGALOPTERA			
Chauliodes sp.	2.8	33	Parsons 1968; Warner 1971
Sialis sp.	2.8	33	Parsons 1968; Warner 1971
DIPTERA			
Ceratopogonidae			
Probezzia sp.	-	-	Parsons 1968
Culcidae			
Chaoborus sp.	4.45	-	Roff and Kwiatkowski 1977
Corethra sp.	≤4.9	-	Lackey 1938
Heleidae palpomyia sp.	4.05	-	Roff and Kwiatkowski 1977
Sphaeromias sp.	4.55	-	Roff and Kwiatkowski 1977
Tabanidae			
Tabanus sp.	-	-	Parsons 1968
Psychodidae			
Psychoda sp.	3.3	13	Warner 1971
Tendipedidae			
Chironomus sp.	2.8	33	Lackey 1938; Warner 1971; Roff and Kwiatkowski 1977
C. plumosus group L.	4.05	-	Roff and Kwiatkowski 1977
C. riparius	2.8	18	Havas and Hutchinson 1983
Cryptochironomus sp.	4.55	-	Roff and Kwiatkowski 1977
Heterotanytarsus sp.	4.55	-	Roff and Kwiatkowski 1977
Phaenospectra sp.	4.05	-	Roff and Kwiatkowski 1977
Procladius sp.	4.45	-	Parsons 1971; Roff and Kwiatkowski 1977
Protanypus sp.	4.05	-	Roff and Kwiatkowski 1977
Tanytarsus sp.	4.45	-	Roff and Kwiatkowski 1977
Tipulidae			
Eriocera sp.	3.5	15	Warner 1971
Pedicia sp.	3.5	8	Warner 1971
Pseudolimnophila sp.	low	high	Parsons 1968
Tipula sp.	3.5	15	Warner 1971

1982). Both Chaoborus and Chironomus species are known to be present in moderately acidic lakes. Reduced predation from fish may actually enhance their success, as they do not appear to be physiologically sensitive to either low pH or high aluminum concentrations.

Hall (1985) compared the response of macroinvertebrates to short-term stream acidification at two sites, one which receives acidic precipitation (Dorset) and one which does not (Experimental Lakes Area, ELA). The macroinvertebrates generally appeared to be far more sensitive to elevated aluminum and H^+ concentrations at ELA (reference site) than at Dorset. Hall (1985) suggested that organisms may have already adapted to elevated acidity and aluminum concentrations at the Dorset site.

3.6.3 ALUMINUM CONTENT

Krantzberg (1985) reported average aluminum concentrations in insect larvae (Diptera, Anisoptera, Trichoptera) of less than 90 $\mu g \cdot g^{-1}$ to more than 290 $\mu g \cdot g^{-1}$. Larvae collected from soft-water lakes (pH 5.4-6.0) in the Muskoka-Haliburton region had higher concentrations of aluminum than those collected from lakes (pH 4.4) in the Wanapitei region. Aluminum concentrations in adult insects were similar for the two sites. Aluminum concentrations within any one taxon were highly variable.

Sadler and Lynam (1985) analyzed the mineral content of stream-dwelling invertebrates (Trichoptera, Ephemeroptera, Plecoptera, Chironomidae and Gammarus) from Wales, U.K. They found that aluminum concentrations in the invertebrates ranged from 100 to 4900 $\mu g \cdot g^{-1}$ (dry weight), and that there was no relationship between the aluminum concentrations of the invertebrates and the pH or aluminum or calcium concentrations in the stream water.

In Diptera larvae, aluminum has been found associated with the anal papillae. These anal papillae are important sites for the active uptake of salts from the environment (Havas 1985b).

3.7 ROTIFERS

Some species of rotifers appear to be particularly aluminum- and acid-tolerant. At the Smoking Hills, in some extremely acidic ponds (pH 2.8 and 18 $mg \cdot L^{-1}$ Al), Brachionus urceolaris was particularly abundant (Havas and Hutchinson 1983). This species has been reported in acidic volcanic lakes (Negoro 1939; Uéno 1958) and in acid mine drainage ponds (Campbell et al. 1964; Parsons 1968), both of which should have elevated levels of aluminum by virtue of their low pH. Other rotifers at the Smoking Hills included Lecane closterocera and an unidentified Bdelloid species (Havas 1980). In addition to B. urceolaris, B. havanaensis, Keratella quadrata, Rattulus latus, and Monostyla bula were recorded in acid mine drainage ponds by Parsons (1968). In less extreme but still moderately acidic environments, Bleiwas (1983) found species of *Asphlanchna*, *Kellicottia*, and *Keratella*. Many of the species presented in Table 3-9 are found in lakes that have H^+ (below pH 4.6) and aluminum (greater than 0.4 $mg \cdot L^{-1}$) concentrations that are toxic to many species of fish.

3.8 FUNGI AND BACTERIA

For the fungus *Neurospora tetrasperma*, there is some evidence that pH influences aluminum toxicity. $Al_2(SO_4)_3$ (0.65 $mg \cdot L^{-1}$ Al) added to a nutrient solution (see Ko and Hora 1972, cited by Burrows 1977, for details) completely inhibited germination at pH 4.8, but had little effect (5% inhibition) at pH 7.0. Other studies that tested the effect of several hundred milligrams of aluminum per litre have little relevance to field conditions and are not presented here.

For bacteria, aluminum toxicity is also pH-dependent. Aluminum applied to growing bacterial cultures induced a pronounced polymorphism at pH 5, but had no obvious effect between pH 6 and 8 (Leppard *et al*. 1985).

Experiments with the bacterium *Escherichia coli* showed that 100 $mg \cdot L^{-1}$ Al as Al^{3+} had no observable effect, whereas Al^{3+}-EDTA (concentrations not provided) at pH 6-8 had exceptional antibacterial activity (Ujiie 1959, cited by Burrows 1977; Meinck *et al*. 1968, cited by Burrows 1977). Unfortunately, the type of substrate was not provided in these studies.

Pseudomonas stutzeri had only a 5% survival rate when exposed to 1.0 $mg \cdot L^{-1}$ Al, added as $AlCl_3$ at pH 4.5 (Zwarun and Thomas 1973). An acetate buffer was used in this experiment, which probably altered aluminum availability.

Experiments on sewage bacteria growing in a nutrient substrate (Aoyagi *et al*. 1972) revealed that growth in the presence of 3% Al, added as aluminum metal, was either accelerated (*Micrococcus caseolyticus*, *Pseudomonas aeruginosa*), inhibited (*Alcaligenes faecalis*), or not affected (*Aerobacter aerogenes*, *Bacillus cereus* var. *mycoides*). Concentrations of aluminum were very high in this study, but because the pH was not indicated, it is not possible to know how much of that aluminum was available to the biota.

Because bacteria and fungi play an important role in decomposition of organic matter and are key factors in nutrient cycling, it would be valuable to learn how aluminum affects their activity in natural environments.

3.9 AMPHIBIANS

Clark and LaZerte (1985) examined the effect of aluminum on the eggs and tadpoles of *Bufo americanus* and *Rana sylvatica*. They found that

Table 3-9. Minimum pH and maximum aluminum concentrations at which rotifers have been recorded in North America.

Species	Minimum pH	Maximum Al concentration ($\mu g \cdot L^{-1}$)	References
Asplanchna priodonta	4.55	-	Roff and Kwiatkowski 1977
Brachionus urceolaris	2.8	18 000	Negoro 1939; Uéno 1958; Parsons 1968; Havas 1980
B. havanaensis	-	-	Parsons 1968
Conochiloides spp.	4.62	440	Ministry of the Environment 1982a, b
Euchlanis spp.	4.62	440	Ministry of the Environment 1982a, b
Filinia spp.	4.62	440	Ministry of the Environment 1982a, b
Gastropus stylifer	3.96	397	Ministry of the Environment 1982a, b
Kellicottia bostoniensis	4.05	440	Roff and Kwiatkowski 1977; Ministry of the Environment 1982a, b
K. longispina	3.98	440	Roff and Kwiatkowski 1977; Ministry of the Environment 1982a, b
Keratella cochlearis	3.98	440	Roff and Kwiatkowski 1977 Ministry of the Environment 1982a, b
K. cochlearis v. *hispida*	4.05	-	Roff and Kwiatkowksi 1977
K. hiemalis	4.05	381	Roff and Kwiatkowski 1977; Ministry of the Environment 1982a, b
K. quadrata	4.1	440	Parsons 1968; Roff and Kwiatkowski 1977; Ministry of the Environment 1982a, b
K. taurocephala	4.05	440	Roff and Kwiatkowski 1977; Ministry of the Environment 1982a, b
Lecane closterocerca	2.8	18 000	Havas 1980
L. luna	4.62	440	Ministry of the Environment 1982a, b
Lecane spp.	4.1	381	Ministry of the Environment 1982a, b
Monostyla bulla	-	-	Parsons 1968
M. lunaris	4.05	440	Roff and Kwiatkowski 1977; Ministry of the Environment 1982a, b
Notholca squamula	4.45	-	Roff and Kwiatkowski 1977
Polyarthra dolichoptera	4.45	-	Roff and Kwiatkowski 1977
P. euryptera	4.1	381	Roff and Kwiatkowski 1977; Ministry of the Environment 1982a, b
P. vulgaris	4.1	440	Ministry of the Environment 1982a, b
Rattulus[α] *latus*	-	-	Parsons 1968
Synchaeta pectinata	4.1	440	Ministry of the Environment 1982a, b
Synchaeta spp.	3.96	440	Ministry of the Environment 1982a, b
Trichocera cylindrica	4.05	440	Roff and Kwiatkowski 1977; Ministry of the Environment 1982a, b
T. multicrinis	3.96	440	Ministry of the Environment 1982a, b
Trichocera spp.	4.1	440	Ministry of the Environment 1982a, b

[α] Renamed *Trichocerca*.

tadpoles could tolerate up to 0.2 $mg \cdot L^{-1}$ Al and pH as low as 4.14, but that the eggs were extremely sensitive. Concentrations of inorganic monomeric aluminum as low as 0.01 $mg \cdot L^{-1}$ at pH 4.32 and 0.02 $mg \cdot L^{-1}$ at pH 4.14 decreased hatching success in B. americanus and R. sylvatica, respectively. Another important finding of this study was that toxicity was not dependent on aluminum speciation, because similar concentrations of Al^{3+} and $Al(OH)_x$ complexes that were toxic at pH 4.14 were not toxic at pH 4.75. Also, AlF_x complexes were as toxic as Al^{3+} and $Al(OH)_x$.

In another study (Clark and Hall 1985), the effects of pH, aluminum, and DOC on the survival of the two species mentioned above as well as Ambystoma maculatum were assessed. The results suggested that the least sensitive species to pH and aluminum was R. sylvatica. Maximum toxicity occurred in the presence of Al^{3+} and AlF complexes.

3.10 FISH

3.10.1 LETHAL CONCENTRATIONS

Aluminum toxicity is affected by a number of variables, including the chemistry of the water; the form(s) of aluminum present; the duration of exposure; whether there was pre-exposure to aluminum; the rate of change in the aluminum concentration; physical factors, such as temperature; and the species and life stages exposed. Toxic concentrations of aluminum can be as low as 0.07 $mg \cdot L^{-1}$ (Kramer and Hummel 1985; Neville 1985), although acute lethal concentrations are generally above 0.2 $mg \cdot L^{-1}$ (Schofield 1977; Dickson 1978a; Fivelstad and Leivestad 1984; Rosseland and Skogheim 1984) in soft water.

Toxic concentrations of aluminum reported for freshwater fishes are highly variable (Table 3-10). Aluminum concentrations that are lethal within 48 h range from 0.2 to 39 $mg \cdot L^{-1}$. Some of the early data (Table 3-10) suggest that concentrations of aluminum that are now encountered in acidified lakes would be toxic only to stickleback (Gasterosteus aculeatus) and eel (Anguilla japonica). More recent studies performed in the field and in the laboratory (Table 3-10) indicate that this is not the case. One possible reason for this discrepancy is that hard water was used in most of the early experiments, and calcium has long been known to reduce metal toxicity. Reduction of aluminum toxicity in brown trout (Salmo trutta) by calcium has been suggested by the work of Muniz and Leivestad (1980b) and Brown (1981, 1983). Also, lack of pH control is a major problem for the interpretation of some of these earlier results.

More recent studies indicate that considerably lower concentrations of aluminum are toxic to freshwater fishes inhabiting soft water (Table 3-11). These toxic concentrations, which range from less than 0.1 to 1.0 $mg \cdot L^{-1}$, commonly occur in acidified lakes and streams and thus pose a serious threat to freshwater fishes. It should be noted that fish can detect and actively avoid lethal concentrations of both aluminum and

Table 3-10. Acute toxicity of aluminum to freshwater fishes in hard water (from Burrows 1977).

Fish	Water	Agent	Al concentration ($mg \cdot L^{-1}$)	pH	Effect	Reference
Killifish (Fundulus heteroclitus)	Hydrant$^{\alpha}$	$Al_2(SO_4)_3$	2.2^{β}	-	Lethal in 36 h	Thomas 1915
	Hydrant$^{\alpha}$	$Al_2(SO_4)_3$	1.1^{β}	-	Lethal in 5 d	Thomas 1915
Goldfish (Carassius auratus)	Tap; 64-80 ppm total hardness	$Al_2(SO_4)_3 \cdot 18H_2O$	8^{β}	5.6	Survival >7 d	Sanborn 1945
		$Al_2(SO_4)_3 \cdot 18H_2O$	20^{β}	4.5	Lethal in 15-24 h	Sanborn 1945
	Tap	$AlCl_3$	>0.5	Unbuffered	Lethal	Minkina 1946
	-	$AlK(SO_4)_2$	26.1	-	Lethal	Penny and Adams 1863
	Hard	$AlK(SO_4)_2$	10.5	5.5	Lethal in 1-10 h	Ellis 1937
	Hard	$AlK(SO_4)_2$	10.5	6.8	Lethal to most in 12-96 h	Ellis 1937
	Hard	$AlK(SO_4)_2$	1.0	7.6	Not lethal in 4 d	Ellis 1937
	-	$AlCl_3$	1350	-	Lethal in 2 h	McGuigan 1927
(Carassius auratus + Carassius carassius)	ns$^{\alpha}$	$Al_2(SO_4)_3$	3700	4-6	Lethal in 30 min	Teulon and Simeon 1966
	ns	$Al_2(SO_4)_3$	2700	4-6	Lethal in 50 min	Teulon and Simeon 1966
	ns	$Al_2(SO_4)_3$	1800	4-6	Not lethal in 1 h	Teulon and Simeon 1966
	ns	AlF_3	450	5.6-6	Lethal in 30 min	Teulon and Simeon 1966
	ns	AlF_3	380	5.6-6	Not lethal in 1 h	Teulon and Simeon 1966
	ns	$Al(NO_3)_3 \cdot 9H_2O$	2200	ca. 4	Lethal in 20 min	Teulon and Simeon 1966
	ns	$Al(NO_3)_3 \cdot 9H_2O$	1450	ca. 4	Lethal in 45 min	Teulon and Simeon 1966
	ns	$Al(NO_3)_3 \cdot 9H_2O$	1100	ca. 4	Not lethal in 1 h	Teulon and Simeon 1966
	ns	$Al_2(SO_4)_3$	56	-	24-h TLM$^{\beta}$ (?)	Kato 1973
Largemouth bass (Micropterus salmoides) Unspecified	Tap; 60-80 ppm total hardness	$Al_2(SO_4)_3 \cdot 18H_2O$	8^{β}	5.6	Not lethal in 7 d	Sanborn 1945
		$Al_2(SO_4)_3 \cdot 18H_2O$	20^{β}	4.5	Lethal in 8-23 h	Sanborn 1945
Bluegill (Lepomis macrochirus)	Tap; 60-80 ppm total hardness	$Al_3(SO_4)_3 \cdot 18H_2O$	8^{β}	5.6	Not lethal in 7 d	Sanborn 1945
Stickleback (Gasterosteus aculeatus)	Tap$^{\alpha}$	$Al(NO_3)_3$	0.07	7	Minimum lethal dose	Jones 1939, 1964; Murdock 1953
	Tap$^{\alpha}$	$Al(NO_3)_3$	0.1	6.6	Average survival, 7 d	Jones 1939, 1964; Murdock 1953
	Tap$^{\alpha}$	$Al(NO_3)_3$	0.13	6.0	Average survival, 4 d	Jones 1939, 1964; Murdock 1953
	Tap$^{\alpha}$	$Al(NO_3)_3$	0.2	5.5	Average survival, 2 d	Jones 1939, 1964; Murdock 1953
	Tap$^{\alpha}$	$Al(NO_3)_3$	0.3	5.2	Average survival, 1 d	Jones 1939, 1964; Murdock 1953

Table 3-10. (Cont'd)

Fish	Water	Agent	Al concentration ($mg \cdot L^{-1}$)	pH	Effect	Reference
Rainbow trout (*Salmo gairdneri*)	Tap	$AlCl_3$	5.2	9.0	TL_{50},[γ] 3 d	Freeman and Everhart 1971
	Tap	$AlCl_3$	5.2	8.5	TL_{50}, 8 d	Freeman and Everhart 1971
	Tap	$AlCl_3$	5.2	8.0	TL_{50}, 32 d	Freeman and Everhart 1971
	Tap	$AlCl_3$	5.2	7.0	TL_{50}, 39 d	Freeman and Everhart 1971
	-	$Al_2(SO_4)_3$	5	-	Serious injury in 5 min	Ebeling 1928
	-	$Al_2(SO_4)_3$	1	-	No effect	Ebeling 1928
Trout Unspecified	Tap	$Al(NH_4)(SO_4)_2$	60	-	Float on side in 10 h	Weigelt *et al*. 1885
	-	$AlK(SO_4)_2$	57	-	Lethal in 15 h	Weigelt *et al*. 1885
California salmon	Tap; 42 ppm alkalinity	$Al_2(SO_4)_3 \cdot 18H_2O$	17	7.3	No effect in 1 h	Schaut 1939
Minnow Unspecified	-	$AlK(SO_4)_2$	10.5	-	Lethal	Ellis 1937
Mosquitofish (*Gambusia affinis*)	Turbid[α]	$AlCl_3$	27	4.3-7.2	96-h TLM	Wallen *et al*. 1957
	Turbid[α]	$AlCl_3$	27	4.3-7.2	48-h TLM	Wallen *et al*. 1957
	Turbid[α]	$AlCl_3$	29	4.3-7.2	24-h TLM	Wallen *et al*. 1957
	Turbid[α]	$Al_2(SO_4)_3$	37	4.4-7.7	96-h TLM	Wallen *et al*. 1957
	Turbid[α]	$Al_2(SO_4)_3$	38	4.4-7.7	48-h TLM	Wallen *et al*. 1957
	Turbid[α]	$Al_2(SO_4)_3$	69	4.4-7.7	24-h TLM	Wallen *et al*. 1957
Eel (*Anguilla japonica*)	ns	$AlCl_3$	0.27	-	Not lethal in >50 h	Oshima 1931
	ns	$AlCl_3$	2.7	-	Lethal in 3.6 h[δ]	Oshima 1931
Japanese killifish	ns	Al^{3+}	4	6.3-7.8	Not toxic	Tabata 1969
Goby	ns	$Al(OH)_3$	70	7-1	Not toxic	Tabata 1969

[α] Hardness of water not specified.

[β] Author's dose data ambiguous.

[γ] Concentration of aluminum resulting in death of 50% of test fish within stated time.

[δ] Average.

Table 3-11. Acute toxicity of aluminum to freshwater fishes in soft water.

Species	pH	Aluminum concentration ($mg \cdot L^{-1}$)	Effect	Reference
Most fish	-	0.2-0.6	Mortality	Dickson 1978a
Brook trout (*Salvelinus fontinalis*)	4.4-5.9	0.25-1.0	Mortality	Schofield 1977
Brook trout (*Salvelinus fontinalis*)	4.2	0.1	Mortality	Hutchinson and Holtze 1985
Atlantic salmon (*Salmo salar*) Sea trout/brown trout Brook trout (*Salvelinus fontinalis*)	4.9-5.0	0.13-0.462	Loss of plasma Cl; buildup of mucus	Rosseland and Skogheim 1984
Brown trout (*Salmo trutta*)	5.0	0.45	Mortality, 48-h	Rosseland 1980
Brown trout (*Salmo trutta*)	-	0.15	Stress symptoms	Muniz and Leivestad 1980b
Rainbow trout (juvenile) (*Salmo gairdneri*)	6.1	0.75 labile inorganic	75% mortality within 4 d, asphyxia;	Neville 1985
	5.0		only slight effect of Al;	
	4.5		90% mortality within 7 d, ionic and osmotic imbalance;	
	4.0[α]		65% mortality within 7 d, ionic and osmotic stress	
Cisco (*Coregonus albula*)	4.9-6.0	<0.9	Mortality	Grahn 1980
White sucker (*Catostomus commersoni*)	-	0.06	Survival >5 d	Baker 1981
		0.15	3.5 d	
		0.22	2 d	
		0.38	1.5 d	
Shiner minnow (*Notropis cornutus*)	5.0	0.07-0.16	50-100% mortality within 7 d; thickening of gill mucous layer	Kramer and Hummel 1985

[α] Al doubled survival time at this pH.

hydrogen ions (Gunn and Noakes 1985). They can thus avoid some of the more acidic streams for spawning and are able to swim to refugia in lakes where they exist.

It appears that lethal concentrations of aluminum are considerably higher in the marine environment (greater than 18 $mg \cdot L^{-1}$, although not all of this is necessarily soluble (Table 3-12; Pulley 1950, cited by Burrows 1977)) than in soft-water lakes and streams (less than 0.3 $mg \cdot L^{-1}$). However, because aluminum concentrations are very low in salt water (approximately 0.002 $mg \cdot L^{-1}$; Bowen 1979), aluminum is unlikely to become a major marine toxicant.

3.10.2 SUBLETHAL SYMPTOMS AND CONCENTRATIONS

Symptoms of aluminum stress in freshwater fish include lack of appetite, listlessness, loss of fright reaction, loss of negative phototaxis, loss of equilibrium, darkening coloration (Freeman and Everhart 1971), gill necrosis, brain demyelination, liver necrosis, kidney inflammation, skin hyperplasia (Spry _et_ _al_. 1981), irregular operculum movement, mucus on gills (Schofield 1977), decrease in growth (Baker 1981), hyperventilation, coughing, respiratory stress, lower blood oxygen tension, and decrease in plasma Cl^- (Muniz and Leivestad 1980a). However, at least some of these symptoms can be induced by elevated H^+ concentrations, as well as by sublethal concentrations of other toxic metals (Schofield 1977). Furthermore, any combination of these symptoms can be observed in aluminum-exposed fish.

Sublethal effects on brook trout (_Salvelinus_ _fontinalis_) are observed in acidic soft water at aluminum concentrations between 0.1 and 0.3 $mg \cdot L^{-1}$ (Schofield 1977). These stress symptoms, however, are pH-dependent. Gill damage, for example, was observed in brook trout exposed to 0.5-1.0 $mg \cdot L^{-1}$ Al above pH 4.4, but not at pH 4.0. Similar pH effects were observed when mucus production on the gills was induced by aluminum (0.25 $mg \cdot L^{-1}$). Growth (i.e., length) of brook trout after 14 d of exposure to 0.1 $mg \cdot L^{-1}$ Al (compared with 0 $mg \cdot L^{-1}$) was reduced at pH 4.9, but not at pH 5.2 (Baker 1981). Pigmentation, cessation of feeding, and listlessness are also symptoms of acid stress, and can be observed in the absence of aluminum below pH 4.4 (Schofield 1977).

In alkaline water, sublethal effects of aluminum on rainbow trout (_Salmo_ _gairdneri_) were observed at 0.52 $mg \cdot L^{-1}$ after 3 to 6 weeks of exposure (Everhart and Freeman 1973). Rainbow trout demonstrated normal behavior and good growth at 0.05 $mg \cdot L^{-1}$ dissolved aluminum. According to Everhart and Freeman (1973), "safe" concentrations of either suspended or dissolved aluminum were less than 0.5 $mg \cdot L^{-1}$ in neutral or alkaline water.

Concentrations of aluminum that have been demonstrated to produce sublethal effects in laboratory fish are common in acidified soft-water lakes (see Chapter 2). Seventy percent of the La Cloche lakes (Canada) have

Table 3-12. Acute toxicity of aluminum[α] to marine fishes[β] (data from Pulley 1950, cited by Burrows 1977).

Fish	Al concentration ($mg \cdot L^{-1}$)	pH	Effect
Speckled trout (*Cynosclon nebulosis*)	9	6.1-7.5	Not lethal in 14 d
	18	5.5-6.7	Lethal in 7 d
	36	4.8	Lethal in 30 min
Redfish (*Sciacnops ocellatus*)	9	6.1-7.5	Not lethal in 11 d
	18	5.1-5.6	Lethal in 0.5-2 h
	36	4.8	Lethal in 45 min
Killifish (*Fundulus grendis*)	18	5.1-6.8	Not lethal in 11 d
	27	4.9-5.0	Lethal in 4-96 h
	36	4.6-4.8	Lethal in 4-24 h
(*Fundulus simulis*)	9	6.1-7.5	Not lethal in 11 d
	18	5.5-6.7	Lethal in 8 d
	36	4.9-5.0	Lethal in 4-96 h
Sheepshead minnow (*Cyprinodon variegatus*)	9	6.1-7.5	Not lethal in 11 d
	18	5.5-6.7	Lethal in 9 d
	36	4.6-5.0	Lethal in 1 d
Mullet (*Mugil cephalus*)	18	5.5-5.6	Lethal in 1 d
	27	4.6-5.0	Lethal in 1 d
	36	4.9-5.0	Lethal in 4 h

[α] Agent was aluminum chloride.

[β] No more than three fish used in any test.

surface water aluminum concentrations in excess of 0.1 mg•L^{-1} (Harvey and Lee 1980, cited by Harvey *et al.* 1981). Ramse Brook (Sweden) has aluminum concentrations between 0.15 and 0.25 mg•L^{-1} and pH between 4.5 and 4.9 (Muniz and Leivestad 1980a). During spring, aluminum concentrations in stream water in the Adirondacks (U.S.A.) can vary from 0.17 to more than 0.6 mg•L^{-1} (Schofield 1977). Brook trout exposed to spring meltwater containing 0.32 mg•L^{-1} Al were stressed and killed, whereas those exposed to 0.17 mg•L^{-1} Al showed no symptoms of aluminum stress (Schofield 1977).

3.10.3 PHYSIOLOGICAL AND BIOCHEMICAL RESPONSES

The physiological and biochemical responses of fish to aluminum are likely to be complicated by the different forms of aluminum present in freshwater environments. Metal toxicity is related to the ionic state of the metal ion. Aluminum(III) (Al^{3+}) should react differently than $Al(OH)_2^+$, $Al(OH)_2^+$, $Al(OH_3)(s)$, and $Al(OH)_4^-$. In most cases, the lower the valency, the more reactive and toxic a metal can be (e.g., Cu^+ vs. Cu^{2+}).

Nieboer and Richardson (1980) classified metals according to their binding preference (Figure 3-3). The most toxic metals (i.e., Au^+, Ag^+, Hg^{2+}, Pb^{2+}, Cu^+) have a high covalent index and a low ionic index. These are commonly referred to as class B metals, and bind preferentially with S and N groups. Aluminum, in contrast, has a high ionic index and a low covalent index. It is listed as a member of class A metals, which are frequently attached to ligands containing oxygen. Because of the different binding preferences, the biochemical and physiological responses to these two classes of metals are likely to be very different.

The effect of aluminum is determined by which species of aluminum are present. Maximum aluminum toxicity for some fishes occurs between pH 5.0 and 5.5. Within this pH range, aluminum exists predominantly as a monovalent cation ($Al(OH)_2^+$) or as a neutral molecule ($Al(OH)_3$). Based on toxicological results, neutral inorganic molecules should have little effect on biota, as chemically they are relatively inactive. Leivestad (1985) found that mortality and ionic regulation failure in Atlantic salmon (*Salmo salar*) were correlated with ion-exchangeable aluminum, and that $Al(OH)_3$ had low toxicity. It has also been shown that aluminum, complexed with F^- or organics, is less toxic than free Al ions (Baker and Schofield 1980).

Neville (1985) showed that 0.075 mg•L^{-1} of labile inorganic aluminum was toxic to juvenile rainbow trout, and that the toxic action varied with pH. At pH 6.1, mortality was rapid (75% mortality within 4 d) and was attributed to asphyxiation, presumably as a consequence of aluminum precipitating onto the gills. At pH 5.0, the toxicity was reduced, but it increased again at pH 4.5 (90% mortality within 7 d) and was attributed to ionic and osmotic imbalance. At pH 4.0, aluminum protected the fish and prolonged survival. The results from this experiment were quite different from results from experiments at higher aluminum concentrations. Neville (1985) stated that at higher aluminum concentrations the monocationic

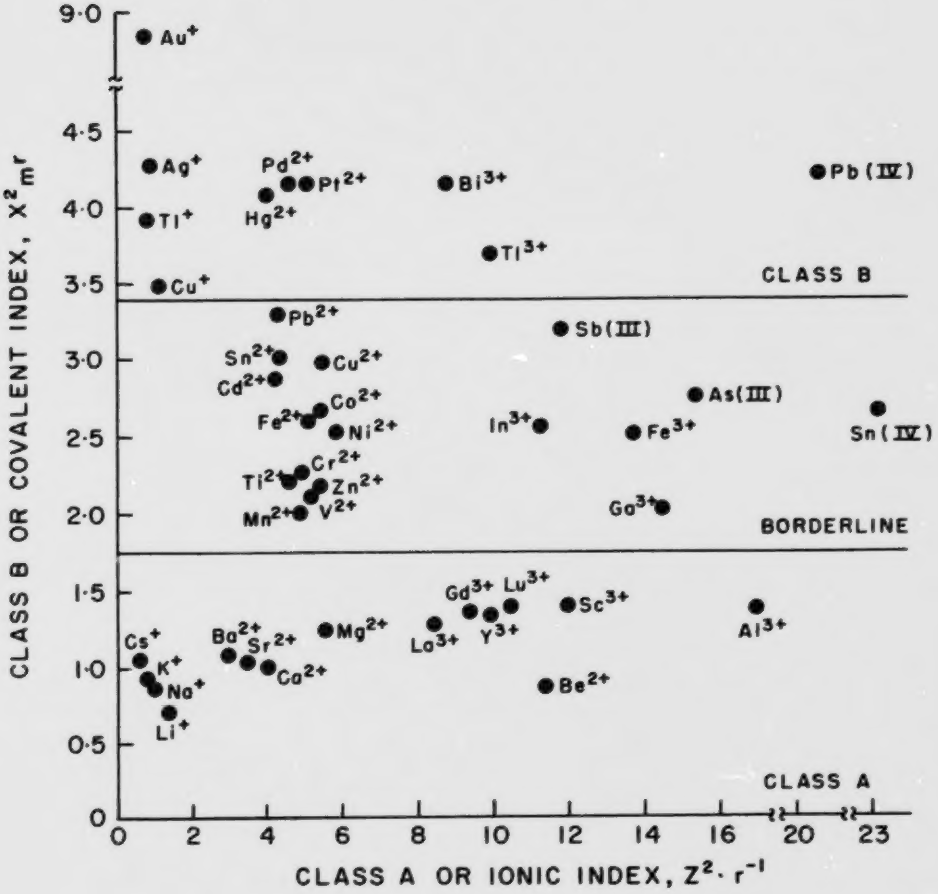


Figure 3-3. Ionic and covalent indices for metal ions (from Nieboer and Richardson 1980).

species $Al(OH)_2^+$ would predominate and would increase toxicity at pH 5.0 instead of pH 4.5 as in her experiment. Also, much of the aluminum, if initially present at higher concentrations, would precipitate out of solution at pH 6.2 and thus not be particularly toxic.

The aluminum content of fish gills is significantly higher in aluminum-exposed fish than in controls (Grahn 1980; Harvey et al. 1981), and the major site of aluminum toxicity appears to be at the gill surface. Aluminum uptake and localization within fish tissue is pH-dependent. At pH 5.2 (1 $mg \cdot L^{-1}$ Al), only the gills of rainbow trout (Salmo gairdneri) had high concentrations of aluminum (approximately 4 $\mu g \cdot L^{-1}$). At pH 6.5 (1 $mg \cdot L^{-1}$ Al), elevated concentrations of aluminum were found in the gastrointestinal tract, which indicates ingestion of presumably particulate aluminum from the test water (Lee and Harvey 1985).

A live-cage technique that can be used to determine if aluminum is present at toxic concentrations in a river or lake has been suggested by Harvey and McArdle (1985). Rainbow trout (Salmo gairdneri) were held in live cages in Plastic Lake inlet and outlet stream water. The fish exposed to inlet water (pH 4.1 and 0.1 $mg \cdot L^{-1}$ total Al) readily accumulated aluminum on their gills (increase from 20 to 105 $\mu g \cdot g^{-1}$ (dry weight)). These same fish showed a rapid loss of sodium and chloride, which is one symptom of acid and/or aluminum stress. Those fish exposed to outlet water (pH 5.4-5.5, 0.04-0.065 $mg \cdot L^{-1}$ total Al) did not accumulate aluminum.

Fish exposed to aluminum show symptoms of respiratory stress; they hyperventilate, cough, and have lower blood oxygen tension (Muniz and Leivestad 1980a). These problems may be related to the excessive mucus that builds up on the gill surface (Kramer and Hummel 1985). The level of dissolved oxygen may also be an important factor in determining the severity of aluminum effects on fish populations. A closer examination reveals that gill necrosis may also occur with loss of distinct lamellae (Baker 1981; Kramer and Hummel 1985).

Playle (1983) found that at pH 5.0, 0.1 $mg \cdot L^{-1}$ Al was toxic to the common shiner (Notropis cornutus) within 4 to 8 h in a static, acute toxicity experiment. An artificial soft-water, organic-free medium was used in this study. One interesting observation showed that aluminum concentrations in the water decreased steadily while the fish were alive but stabilized once they were dead. This suggests that aluminum may have been taken up actively by the fish.

Kramer and Hummel (1985), also working with the commmon shiner, reported that large individuals were more sensitive than small ones, and that citrate, malate, and fluoride could reduce aluminum-induced mortality. Concentrations of 0.15 $mg \cdot L^{-1}$ Al and higher caused the double epithelial layer of the second lamellae to slough off, exposing the cell-blood channel directly to the environment. At lower aluminum concentrations (0.04-0.12 $mg \cdot L^{-1}$), the second lamellae appeared fused, and the gill mucous layer was noticeably thickened.

Gills function as organs of gas exchange, but are also critical for ion exchange, especially for the uptake of Na^+ and Cl^-. Muniz and Leivestad (1980a) were among the first to show that fish are unable to maintain serum ionic balance following exposure to aluminum. Plasma Cl^- concentrations in brown trout decreased at pH 5.0 and 0.19 $mg \cdot L^{-1}$ Al, but not at 0.035 $mg.L^{-1}$ (Figure 3-4). The maximum decrease of Cl^- occurred at pH 5.1-5.5 with 0.9 $mg \cdot L^{-1}$ Al. Both lower (pH 4.3-4.5) and higher (pH 6.0) pH levels appeared to be less toxic. At pH 4.0, 0.038 $mg \cdot L^{-1}$ Al actually caused a decrease in net loss of plasma Cl^- (Figure 3-5). These results support those previously mentioned by Baker (1981) as well as those mentioned by Havas (1985a) for *Daphnia magna*. As plasma ions decreased, hematocrit increased in Atlantic salmon, sea trout, and brown trout exposed to pH 4.9-5.0 and 0.13-0.462 $mg \cdot L^{-1}$ labile Al (Rosseland and Skogheim 1984).

3.10.4 SPECIES AND AGE-CLASS DIFFERENCES

Fish species differ in their susceptibility to aluminum. When brook trout (*Salmo trutta*) and brown trout (*Salvelinus fontinalis*) were exposed to soft water containing 0.45 $mg \cdot L^{-1}$ Al at pH 5.0, the brown trout were considerably more sensitive than the brook trout to aluminum (Rosseland 1980). All of the brown trout died after a 48-h exposure. The brook trout, in contrast, showed many of the symptoms associated with aluminum stress (increased metabolic rate, hyperventilation), but were able to recover within 12-42 h. The only stress symptom that persisted was excessive mucus on the gills.

More recent studies (pH 4.9-5.0, 0.13-0.462 $mg \cdot L^{-1}$ labile Al) with four species of fish (1- and 2-year-old Atlantic salmon, sea trout, brown trout, and 1-year-old brook trout) indicated that 2-year-old presmolt salmon were the most aluminum-sensitive, whereas brook trout were the most aluminum-tolerant (Rosseland and Skogheim 1984). Loss of plasma chloride was more rapid in salmon, followed by sea trout and brown trout. A comparison of the mortality of eggs and alevins in an acidic brook (pH 4.8-5.0, 0.20-0.31 $mg \cdot L^{-1}$ Al) indicated that mortality of alevins was slightly higher than that of the eggs for sea trout (99.7 vs. 97%), Atlantic salmon (93.2 vs. 57%), brown trout (86.9 vs. 35%), and brook trout (12.9 vs. 8%) (Skogheim and Rosseland 1984). Development from fertilization to initiation of feeding was also delayed in the acidic brook water compared with development in water from a nonacidic lake (pH 6.4-6.8, less than 0.01 $mg \cdot L^{-1}$ labile Al).

A comparison of white sucker (*Catostomus commersoni*) and brook trout showed that the former was considerably more sensitive to both aluminum and low pH (Baker and Schofield 1980). Exposure to 0.2 $mg \cdot L^{-1}$ Al at pH 5.2 resulted in 100 and <20% mortality of white sucker and brook trout sac fry, respectively, at the end of a 14-d experiment (Baker 1981). Swimup fry were more aluminum-tolerant than were sac fry. Under the same conditions, mortality of swimup fry was approximately 60% for white suckers and about 30% for brook trout (Baker 1981).

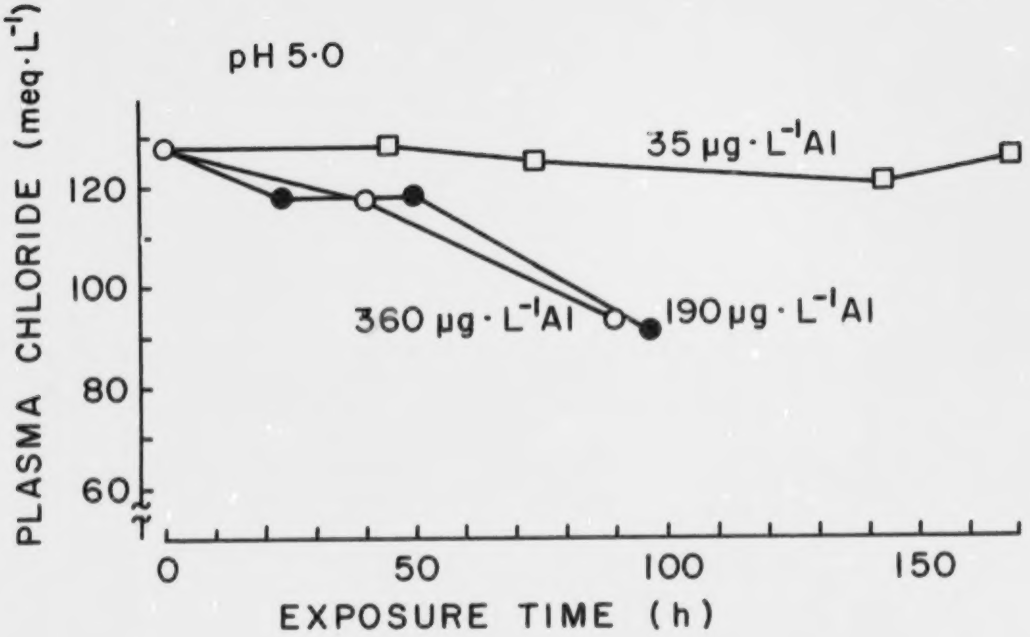


Figure 3-4. Plasma chloride concentrations in brown trout (Salmo trutta) exposed to different aluminum concentrations at pH 5.0 (from Muniz and Leivestad 1980b).

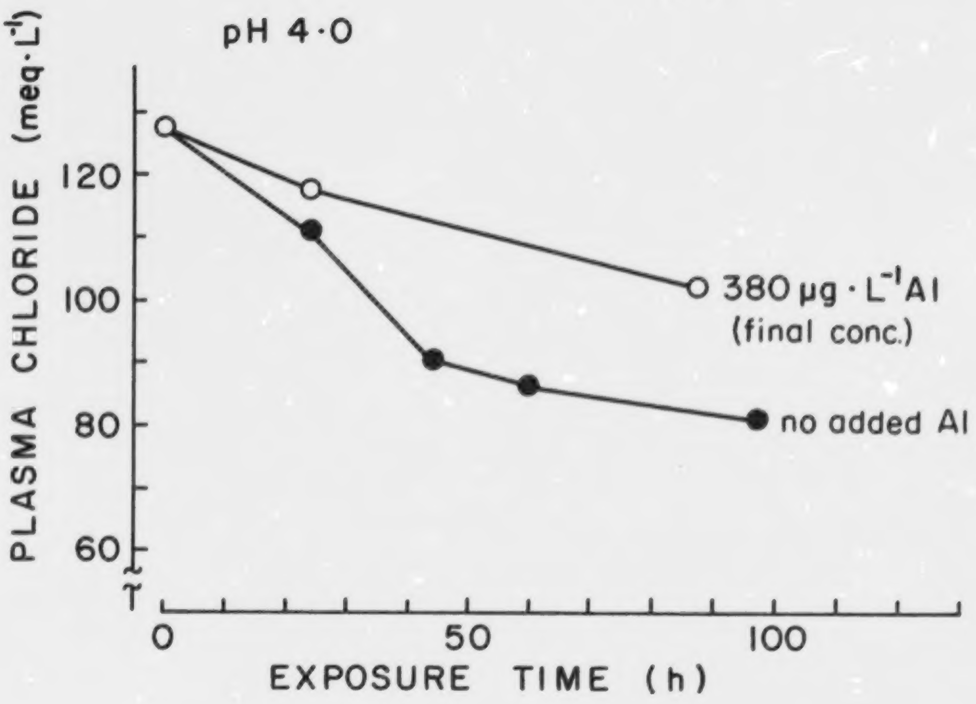


Figure 3-5. Plasma chloride concentrations in brown trout (Salmo trutta) exposed to pH 4.0 with and without aluminum (from Muniz and Leivestad 1980b).

Sensitivity to aluminum can also change with the age and size of fish. Baker (1981) found that brook trout at different stages of development had different survival rates when they were exposed to 0.2 $mg \cdot L^{-1}$ Al at pH 5.2: fingerlings < eggs < sac fry < swimup fry. The order of survival rates for white sucker was: fingerlings < swimup fry < eggs = sac fry. Although white sucker fingerlings were exposed only to pH 4.4 at 0, 0.5, and 0.85 $mg \cdot L^{-1}$ Al, the results indicate that they were more tolerant than the other life stages tested. Rosseland and Skogheim (1984) reported that 2-year-old presmolt salmon were extremely sensitive to aluminum, and that salmon smolts, but not younger fish, showed episodic fish kills in acidic River Vikedal, between 1981 and 1983.

Table 3-13 summarizes the relative sensitivity of the different developmental stages of both brook trout and white sucker to pH and aluminum. This table shows that the response of the embryo to aluminum is quite different from those of the larvae and postlarvae. Survival and growth of the larvae were reduced, whereas those of the embryo improved in the presence of aluminum at low pH. The reason for this reversal is not known.

Everhart and Freeman (1973) found that 5.2 $mg \cdot L^{-1}$ Al was toxic to adult rainbow trout (Salmo gairdneri). There was no evidence of aluminum toxicity to trout roe under the same conditions. Based on the work of Mathews (1904, cited by Burrows 1977), 338 $mg \cdot L^{-1}$ Al was the minimum aluminum concentration preventing the appearance of embryos of killifish eggs.

3.10.5 EFFECTS OF ALUMINUM SPECIATION

One of the earliest and most detailed studies examining aluminum speciation and aluminum toxicity to fish was conducted by Baker (1981). Effects of three species of aluminum (free Al^{3+}, aluminum fluoride, aluminum citrate) on survival and growth of white sucker (Catostomus commersoni) and brook trout (Salvelinus fontinalis) were compared at different pH levels. The maximum aluminum toxicity (0.5 $mg \cdot L^{-1}$ Al) occurred in oversaturated solutions between pH 5.2 and 5.4. At lower pH levels, Al and H ions interacted antagonistically. This antagonism was also reported by Muniz and Leivestad (1980b) for brown trout and more recently by Havas (1985a) for Daphnia magna. The mechanism for Al/H ion antagonism in fishes is not known, but may be similar to that reported for Daphnia magna (Havas and Likens 1985b) (see Section 3.4.4).

One important implication of this relates to liming of acidic lakes. If an acidic lake with elevated concentrations of aluminum is limed, the lake water may become supersaturated with aluminum as the pH approaches and exceeds 5.5. If fish and/or other forms of aquatic animals are still present in that lake, the liming may actually be more harmful than beneficial (Dickson 1978b).

Table 3-13. pH level necessary to prevent measurable (≥ 15%) reduction in survival of early life history stages of brook trout and white suckers assuming no aluminum or aluminum concentrations typical of an Adirondack surface water at that pH level (from Baker and Schofield 1982).

Species	Life history	Desired pH level	
		With no Al	With Al
Brook trout (*Salmo trutta*)	Embryo development through eyed stage	≥ 4.5	≥ 4.1
	Embryo development through hatching	≥ 4.5	≥ 4.1
	Larvae	≥ 4.2	≥ 4.5
	Postlarvae	≥ 3.7	≥ 4.8
White sucker (*Catostomus commersoni*)	Embryo development through eyed stage	≥ 5.6	≥ 5.6 or 4.6-4.8
	Embryo development through hatching	≥ 5.6	≥ 5.6
	Larvae	≥ 5.3	≥ 5.6
	Postlarvae	≥ 4.9	≥ 5.4

Organically bound aluminum was the least toxic of the three species tested (Baker 1981). Aluminum fluoride complexes were more toxic than aluminum citrate complexes but less toxic than free Al^{3+} or aluminum hydroxides (Figure 3-6). This partially explains why fish can survive at elevated aluminum concentrations in acidified humic lakes but not in acidified clear-water lakes. Sensitivity to aluminum increased with the age of fish (Baker and Schofield 1980). Although both aluminum and low pH affected fry weight ($P \leq 0.01$), only aluminum had an effect on fry length ($P \leq 0.05$). Of the two species, white suckers were more sensitive than brook trout to both aluminum and low pH.

3.10.6 ACCLIMATION

Acclimation (a compensatory shift by an organism which alters its zone of tolerance) of different life history stages of brook trout to increased acidity and aluminum levels was examined by Guthrie (1981). In this study, acclimation was both short-term (usually 4-5 d) and dynamic because the "rates of change in water quality must be sufficient to stimulate physiological adjustment, without exceeding the ability of the fish to resist these changes as acclimation occurs" (Schofield et al. 1981). The results indicate that brook trout can acclimate to certain concentrations of aluminum. At pH 4.5 acclimated sac fry survived longer than nonacclimated individuals when exposed to either 0.2 or 0.4 $mg \cdot L^{-1}$ Al (Figure 3-7). At pH 4.0, the hydrogen ion concentration appears to be too toxic for successful acclimation to occur at either aluminum concentration. Acclimated yearlings survived longer than nonacclimated individuals at pH 5.0, but not at pH 4.5 in the presence of 0.4 $mg \cdot L^{-1}$ Al (Figure 3-8).

Acclimation had no consistent effect on growth. Individuals exposed to low pH, however, were smaller than the controls (neutral pH, trace aluminum), indicating that fish were still in a stressful environment.

It is clear from these experiments (Guthrie 1981) that the potential exists for successfully acclimating brook trout to slight increases in acidity and aluminum levels. Practising dynamic acclimation with hatchery-reared fingerlings may significantly increase stocking success in waters of low pH and high aluminum concentrations; however, there are limits to the ability of fish to become acclimated, and this cannot be viewed as a substitute for preventing or minimizing acidification of lakes and streams. These experiments also suggest that the rate of change in pH and aluminum levels in nature may be very important for determining the ability of fish to survive. Rapid changes are more likely to produce greater stress.

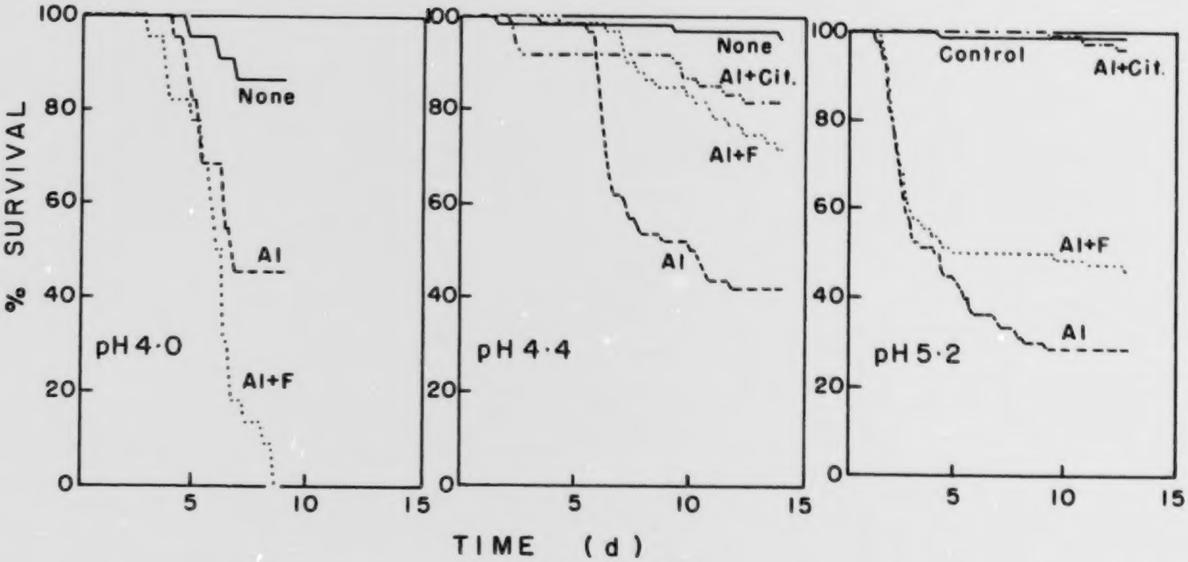


Figure 3-6. Effect of aluminum citrate, aluminum fluoride, and free aluminum on survival of brook trout (*Salvelinus fontinalis*) at different pH levels (from Baker 1981).

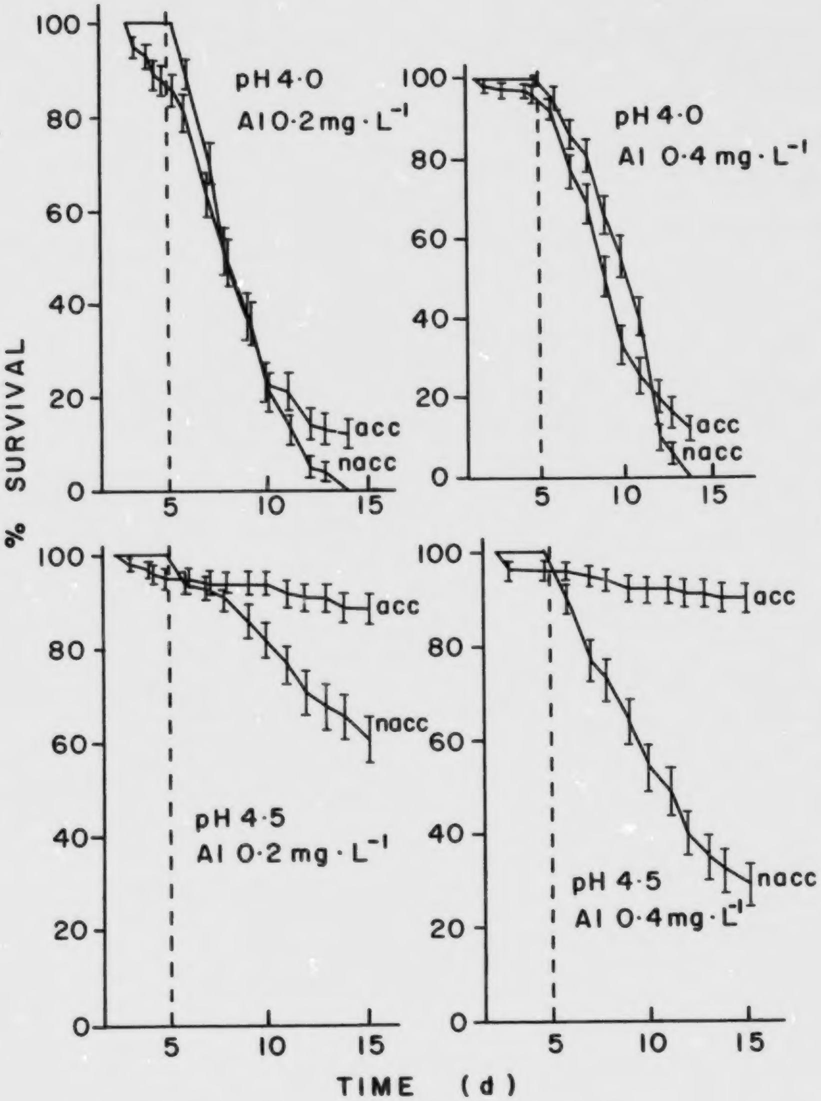


Figure 3-7. Survival of aluminum-acclimated and nonacclimated brook trout (*Salvelinus fontinalis*) sac fry at pH 4.0 and 4.5 at elevated concentrations of aluminum (from Guthrie 1981).

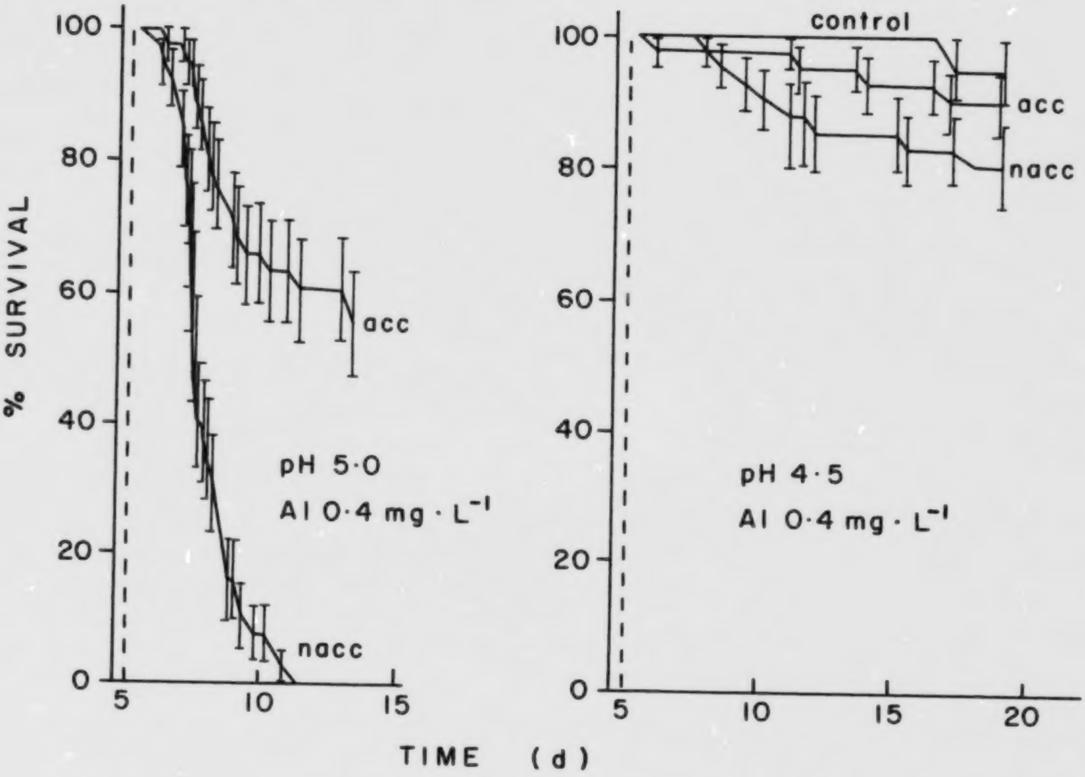


Figure 3-8. Survival of aluminum-acclimated and nonacclimated brook trout (Salvelinus fontinalis) yearlings at pH 4.5 and 5.0 at elevated concentrations of aluminum (from Guthrie 1981).

3.11 BIRDS[α]

High concentrations of aluminum in aquatic ecosystems may affect organisms at higher levels in the food chain in two ways: (i) indirectly, with toxicity to sensitive aquatic biota resulting in loss of prey; and (ii) directly, with increased dietary intake of aluminum resulting in toxicity to the organisms themselves.

Evidence of loss of prey and a decline in numbers of breeding birds around streams with low pH and high aluminum concentrations has been found in Wales (Ormerod *et al*. 1986). Breeding success of dippers (*Cinclus cinclus*) was strongly correlated with the amount of filterable aluminum in streams and the abundance of emerging insects (Trichoptera and Ephemeroptera) and small fish. Those streams without breeding dippers had higher concentrations of aluminum (≥ 0.1 mg.L^{-1} Al), lower mean pH, lower diversity and biomass of Ephemeroptera and Trichoptera, and reduced availability of small fish.

Increased concentrations of aluminum found in emerging insects from acidified aquatic ecosystems (Hall and Likens 1981; Sadler and Lynam 1985) and reports of reproductive impairment in some wild birds nesting in the vicinity of an acidified lake in Sweden (Nyholm 1981) have aroused concern about the toxicity of aluminum to birds. High levels of aluminum were found in the bones of pied flycatchers (*Ficedula hypoleuca*) producing defective eggshells in northern Sweden (Nyholm 1981). The mechanism of effect was postulated as the binding of phosphate by aluminum in the intestinal tract and disturbance of calcium metabolism resulting in decreased apatite deposition in the bone marrow and malformation of eggshells.

Experimental studies with birds have confirmed the increased absorption of aluminum by females during egg formation, as indicated by higher bone aluminum levels (Carrière *et al*. 1986). However, these studies failed to confirm effects on eggshell quality or on overall reproductive performance. No significant influence of dietary aluminum (0.1%) on reproduction or growth of ring doves fed experimental diets with adequate levels of calcium (0.9%) and phosphorus (0.5%) were found. The level of aluminum in the diet was similar to that found in insect prey from areas affected by acidic precipitation (Hall and Likens 1981; Sadler and Lynam 1985; Krantzberg 1985). Although the levels of calcium and phosphorus administered in this experiment were higher than those of aluminum, the effect could well have been greater if these essential minerals were deficient for growth and reproduction (Simkiss 1961).

Relative to that of other metals, the toxicity of dietary aluminum is low (Sorenson *et al*. 1974). In birds, the principal toxic effect seems to be the disturbance of phosphorus metabolism. Aluminum binds

---

[α] This section was written by Kathleen L. Fischer, Canadian Wildlife Service, Environment Canada.

phosphorus in the alimentary canal and forms insoluble compounds, resulting in an imbalance in the ratio of available calcium and phosporus (Ondreicka et al. 1971). In growing and adult birds and in mammals, this can lead to osteomalacia and hypophosphatemia (Elliott et al. 1978a; Lipstein and Hurwitz 1982; Robertson et al. 1983). Consequently, the aluminum concentration necessary to cause an effect could be lower when calcium and phosphorus in the diet are low. Similar interactions between dietary calcium and some other chemicals, such as kepone (Eroshenko and Place 1978) and DDT (Cecil et al. 1973), have been found. In these studies, the toxicity of chemical contaminants increased with decreasing dietary levels of calcium.

Under normal conditions, aluminum is absorbed only to a small extent through the intestinal epithelium (Cam et al. 1976). Absorption of aluminum, along with phosphorus, has been stimulated in chickens by injecting a derivative of vitamin D (Long et al. 1980). In most vertebrates, the synthesis of this substance is mediated by the parathyroid hormone; it is normally produced by the kidneys when the need for calcium increases or when there is a shortage of dietary calcium. The production of $1,25\text{-}(OH)_2D_3$ subsequently increases the synthesis of intestinal calcium-binding proteins which augment the absorption of calcium (Wasserman 1962; Haussler and McCain 1977). These proteins also increase the absorption of metals, such as lead (Shields and Mitchell 1941; Six and Goyer 1970) and cadmium (Washko and Cousins 1977). It has been previously noted that the absorption of many metals is enhanced when the level of vitamin D is high and when the parathyroid activity is increased (e.g., during egg-laying) (Worker and Migicovsky 1961a, b). Mayor et al. (1977) found a similar relationship between the level of parathyroid hormone and the gastrointestinal absorption of aluminum in the rat. Birds stressed by a diet low in calcium and phosphorus may, therefore, be more sensitive to the presence of aluminum in the diet, or may accumulate it to a greater extent. The differences found between field observations and experimental results may be a result of species-to-species variation or the relative availability of aluminum and essential minerals in the diet.

Many areas subjected to acidification and mobilization of aluminum are also areas where the calcium and phosphorus levels in surface waters are low. Under these conditions, it is possible that the availability of aluminum could exceed the availability of the essential minerals in prey organisms, which could cause increased absorption of aluminum and produce physiological damage, including reproductive impairment in predatory wildlife.

4.0 ALUMINUM IN TERRESTRIAL ECOSYSTEMS

B. Freedman[1] and T.C. Hutchinson[2]

[1]Department of Biology and Institute for
Resource and Environmental Studies
Dalhousie University
Halifax, Nova Scotia B3H 4J1

[2]Department of Botany and Institute
for Environmental Studies
University of Toronto
Toronto, Ontario M5S 1A4

4.1 INTRODUCTION

It has long been recognized that acidic soils are detrimental to the growth of plants; in recognition of this fact, farmers have practised liming for hundreds of years. Problems of soil acidity have also been recognized by plant and soil scientists for some time. According to Veitch (1904), there had been a "growing realization of the injury due to acid soils and . . . recognition of the wide-spread occurrence of such soils." Veitch (1904) also noted that he was "dealing with several 'kinds' of acidity which affect fertility very unequally", including acidity resulting from aluminum. Hartwell and Pember (1918) more conclusively identified aluminum as a toxic factor in acidic soils, and investigated the nature of the effect in solution culture. They also noted that the practical advantage of liming and phosphorus fertilization may be because of precipitation of aluminum, rather than just decreased acidity or increased phosphorus supply to the plant. Overall, there was much research on the nature of soil acidity and aluminum toxicity during the first half of the present century, most of it done by agronomists. This topic was recently reviewed from a historical perspective by Hutchinson (1983), and will not be dealt with in detail here.

Despite the rather well-known role of aluminum toxicity in acidic agricultural soils, there has been relatively little appreciation of its importance in acidic natural ecosystems, other than some work associated with the physiological plant ecology of calcicole and calcifuge species (e.g., Rorison 1960a, b; Hackett 1962, 1965, 1967; Clarkson 1966; Grime and Hodgson 1969). However, very little work has been done in forests, or on forest tree species. Recently, as a result of concerns about the ecological impacts of the deposition of acidifying substances from the atmosphere, increased availability of soil aluminum in terrestrial ecosystems has emerged as an important topic. This has stimulated thought and research in two parallel streams: (i) the degree of mobilization of plant-available aluminum in acidic soils and the susceptibility of commercially important plant species to the observed concentrations; and (ii) the possible biogeochemical linkages between the terrestrial and freshwater parts of the watershed, in that the ionic aluminum mobilized in soils may be the source of toxic aluminum in acidic, oligotrophic surface waters (see Chapter 2).

The purpose of the present chapter is to provide a detailed but not exhaustive overview of the understanding of the terrestrial biogeochemistry of aluminum, its mobilization in acidic soils, and its effects on plants.

4.2 TERRESTRIAL BIOGEOCHEMISTRY OF ALUMINUM

Because Al^{3+} and Si^{4+} are similar in size, aluminum ions can substitute for silicon in tetrahedral or octahedral lattices with oxygen; it is in this aluminosilicate form that most crustal aluminum occurs. For example, in typical feldspars some 25-50% of the tetrahedra contain Al^{3+} substituted for Si^{4+} (Hausenbuiller 1978), and, in general, the more abundant primary minerals and some secondary minerals (especially certain clays and aluminum sesquioxides) have high concentrations of aluminum (Table 4-1).

Typical mineral soils have high concentrations of aluminum (overall mean of 104 000 $\mu g \cdot g^{-1}$; median of 71 000 $\mu g \cdot g^{-1}$; range of 10 000 to 300 000 $\mu g \cdot g^{-1}$; after Bowen 1979). In fact, certain highly weathered tropical soils and surface mineral deposits containing a mixture of aluminosilicate clays are mined as bauxite, an aluminum ore (Bailey _et al._ 1978; Bowen 1979). Aluminum can occur in many forms in soils, e.g., as (i) tetra- and octahedral crystals of primary aluminosilicate minerals; (ii) amorphous or crystalline clays and sesquioxides; (iii) aluminum phosphates; or (iv) ionic forms bound to exchange sites on organic matter or clays or in the soil solution (including Al^{3+} at pHs below _ca._ 4.5, but also $AlOH^{2+}$ or $Al(OH)_2^+$ under moderately or mildly acidic conditions, respectively, or $Al(OH)_3$ or $Al(OH)_4^-$ under mildly or strongly alkaline conditions, respectively) (Hausenbuiller 1978).

On a global scale, it has been estimated that some 330 x 10^9 $kg \cdot a^{-1}$ of aluminum are mobilized by weathering processes, 11 x 10^9 $kg \cdot a^{-1}$ reach the oceans via river flow, 134 x 10^9 $kg \cdot a^{-1}$ are mined, and 2.8 x 10^9 $kg \cdot a^{-1}$ are emitted to the atmosphere as a result of the combustion of fossil fuels (Bowen 1979).

The cycling of aluminum in terrestrial ecosystems has not been extensively studied. One of the more detailed investigations was done in the Solling Forest of West Germany, in a beech (_Fagus sylvatica_) and a spruce (_Picea abies_) stand (Table 4-2). Total atmospheric deposition to these stands averaged 2.16 and 2.84 $kg \cdot ha^{-1} \cdot a^{-1}$, respectively, with the difference being the result of the more effective filtering of atmospheric particulates (i.e., dry deposition of aluminum) by the spruce stand. Deposition of aluminum to the forest floor beneath the beech and spruce tree canopy (as bulk-collected throughfall plus stemflow) was 1.75 and 3.01 $kg \cdot ha^{-1} \cdot a^{-1}$, respectively, implying a consumption of 19% of the atmospheric

Table 4-1. Concentrations of aluminum in a range of biogeochemical compartments.

Compartment		Average aluminum concentration (μg·g^{-1} (dry weight))	Reference
Earth's crust		80 000	Bailey *et al*. 1978
		83 600	Fortescue 1980
		82 000	Bowen 1979
		81 000	Hausenbuiller 1978
Specific minerals			
Granite		77 000	Bowen 1979
Basalt		87 600	Bowen 1979
Shale		88 000	Bowen 1979
Limestone		9 000	Bowen 1979
Sandstone		43 000	Bowen 1979
Marine clays		94 000	Bowen 1979
Coal		10 000	Bowen 1979
Fresh water		0.3	Bowen 1979
		0.24	Fortescue 1980
Rainwater		0.16	Fortescue 1980
Soil	average	71 000	Bowen 1979
	range	(10 000-300 000)	
Vegetation			
Bacteria		210	Bowen 1979
Lichens		20-6000	Bowen 1979
Fungi		30-350	Bowen 1979
Bryophytes		500-6000	Bowen 1979
Pteridophytes		230	Bowen 1979
Woody gymnosperms		250-530	Bowen 1979
Woody angiosperms		90-200	Bowen 1979
Herbaceous vegetables		0.1-200	Bowen 1979
Typical land plants		90-530	Bowen 1979
Animal tissues			
Mammal muscle		0.7-28	Bowen 1979
Mammal bone		4-27	Bowen 1979

Table 4-2. Fluxes of aluminum in a beech and a spruce forest in West Germany (modified from Mayer 1983).

Parameter	Flux ($g \cdot ha^{-1} \cdot a^{-1}$)	
	Beech	Spruce
Atmospheric inputs		
Dissolved wet deposition	1 080	1 080
Dry + undissolved wet deposition	1 080	1 760
Total atmospheric inputs	2 160	2 840
Deposition to forest floor below canopy	1 750	3 010
Accumulation from atmospheric deposition		
In forest canopy	600	0
In bark and wood	300	80
Losses from humus layer	2 700	2 400
Losses from mineral soil	12 000	21 000
Output with seepage below rooting zone	15 500	24 000

Note: Data are means over 1974-1978.

aluminum inputs by the beech canopy, and a 6% enhancement by the spruce canopy. Leaching of aluminum by water percolating below the rooting depth was 15.5 and 24.0 kg•ha^{-1}•a^{-1} for the two stands, with most of this (77 and 88%, respectively) mobilized from the acidic mineral soils. Although these losses of aluminum from the rooting soil horizons are large, as a proportion of the total aluminum they are quite insignificant (much less than 0.01%). The net fluxes of aluminum to below the rooting depths of these ecosystems (i.e., inputs minus outputs) were -13.3 and -21.2 kg•ha^{-1}•a^{-1} for the beech and the spruce forests, respectively. This aluminum would be derived from the weathering of minerals.

Another biogeochemical study that collected data on aluminum was done in the Hubbard Brook Experimental Forest, in New Hampshire (Likens et al. 1977; Bormann and Likens 1979). Inputs of aluminum from the atmosphere were considered to occur only in trace quantities, whereas stream-water exports over 12 years averaged 3.4 kg•ha^{-1}•a^{-1} (composed of 2.0 kg•ha^{-1}•a^{-1} as dissolved Al^{3+} and 1.4 kg•ha^{-1}•a^{-1} as particulate aluminum; note that the stream-water export of Al^{3+} was believed to approximate the mobilization of aluminum by the weathering of minerals). The net flux from this largely hardwood forest ecosystem was therefore ca. -3.4 kg•ha^{-1}•a^{-1}, considerably smaller than that calculated for the Solling forests (which did not include particulate export and only considered leaching to below the rooting depth of the mineral soil).

The flux of aluminum from forested watersheds can be influenced by recent disturbances. Likens and Bormann (1972), Bormann et al. (1974), and Likens et al. (1977) reported on a small (17 ha), largely hardwood watershed in New Hampshire in which all of the trees were felled (but left lying on the site), and then herbicides applied for three growing seasons to inhibit regeneration. During this time period, the mean stream-water concentrations of dissolved aluminum averaged 5.2-fold higher in the disturbed watershed (compared with ca. 0.23 µg•mL^{-1} in the uncut watershed stream). This contributed to higher stream-water exports of Al^{3+}, which averaged 21.1 kg•ha^{-1}•a^{-1}, compared with 3.0 kg•ha^{-1}•a^{-1} for the undisturbed watershed. Total stream-water particulate losses were 3200 kg•ha^{-1}•a^{-1} for the disturbed watershed, versus 380 kg•ha^{-1}•a^{-1} for the control watershed. If an aluminum concentration of 8.3% is assumed (this is the mean bedrock concentration of aluminum at Hubbard Brook (Likens et al. 1977)), then the particulate exports represent ca. 267 and 31 kg•ha^{-1}•a^{-1} of aluminum, respectively. Thus, total stream-water exports of aluminum from the disturbed watershed over the first three postdisturbance years averaged 288 kg•ha^{-1}•a^{-1} (93% as particulate aluminum), compared with 34 kg•ha^{-1}•a^{-1} (88% as particulate aluminum) for the undisturbed control watershed.

It is clear that aluminum is very abundant in most terrestrial environments, and its global fluxes are large. However, aluminum has a rather low biological affinity, and it is normally present in both plants and animals in relatively low concentrations (Table 4-1; however, note that certain plants are hyperaccumulators of aluminum, as will be described later). This low biological affinity of aluminum is mainly the result of its low solubility and reduced availability at circumneutral pH (Hutchinson 1945). However, even low concentrations of aluminum can be toxic to organisms, as will be discussed later.

4.3 ALUMINUM AVAILABILITY IN SOILS

In typical soils the aluminum concentration averages 10% by weight (Bowen 1979). Assuming an average bulk density of 1.3 $g \cdot cm^{-3}$ (Russell 1973) and a rooting depth of 50 cm, this represents ca. 7 x 10^6 $kg \cdot ha^{-1}$ of total aluminum. Aluminum is not distributed homogeneously in the soil column, particularly in natural ecosystems with well-developed soil profiles. This was described by Lunt (1932), whose investigations of forest soils indicated relatively low concentrations in the A horizon (a zone of mobilization and downward leaching of aluminum, iron, and organic matter) and relatively high concentrations in the B horizon (a zone of deposition of these materials), whereas the relative concentrations in the parent C horizon were less predictable (Table 4-3). Such a pattern of downward leaching of aluminum into the B horizon and its retention there is typical of podsols. The mobilization is greatest in moist temperate forests on well-drained sites, especially in acidic soils under conifers. Organic acids play an important part in this movement. This contrasts with the situation in the humid tropics, where silicates are leached downward during the process of laterization, leaving behind sesquioxides of iron and aluminum (Russell 1973; Hausenbuiller 1978).

Although this total aluminum is associated with most of the important mineral constituents of the soil, it generally occurs in especially high concentrations in the finer fractions. In another early study, Mirasol (1921) examined the soil size-fraction distribution of total aluminum and found an average concentration of 5.5% in the fine sand, 8.4% in the coarse silt, and 23% in the fine silt-clay fractions.

The great bulk of these large quantities and high concentrations of total aluminum occurs as minerals that are virtually insoluble in the soil solution, and hence are not biologically available. Several factors are known to affect the solubility or exchangeability of ionic aluminum. The most important of these factors is the pH of the soil solution (Figure 4-1); the solubility and toxicity of aluminum (particularly as Al^{3+}) increase greatly at soil pH levels less than ca. 4.5-5.0 (e.g., Mirasol 1921; Magistad 1925; Pierre et al. 1932; Hutchinson 1943, 1945; Pionke and Corey 1967; Coulter 1969; Evans and Kamprath 1970; Richburg and Adams 1970; Blancher and Scrivener 1972; Breemen 1973; Bache 1974; Foy 1974; Misra et al. 1974; Awad et al. 1976; Berg 1978; Bache and Crooke 1981; Bouton et al. 1982; Ulrich 1983; Haynes 1984). Acidic soils with high concentrations of available aluminum exist in a wide variety of locations, including various agricultural soils where acidity is generated by fertilization or cropping, acidic sulfate soils, acidic forest soils, and acid mine spoil or tailings disposal sites. For example, examination of the acidic podsolic soils of a variety of black spruce (Picea mariana) and jack pine (Pinus banksiana)

Table 4-3. Vertical distribution of total aluminum in some typical U.S. forest soils (modified from Lunt 1932).

	Total aluminum concentrations (% dry weight)		
Horizon	Well-developed podsol (n=3)	Moderately developed podsol (n=3)	Mull (n=4)
A	0.6	0.7	1.9
B	2.0	2.3	2.3
C	1.4	2.6	1.5

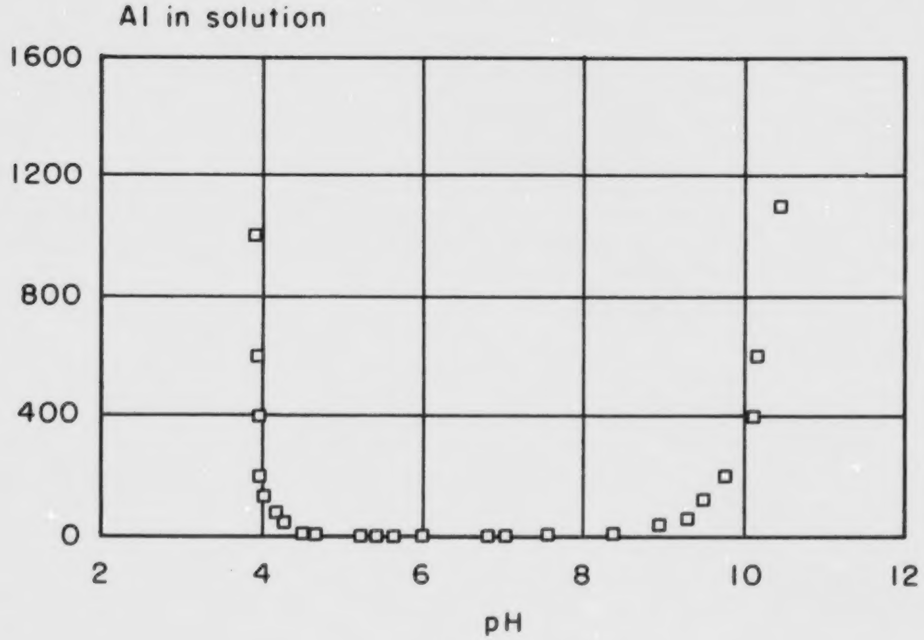


Figure 4-1. Solubility of aluminum in water as affected by pH. This general pattern of aluminum solubility has been confirmed in more recent studies (modified from Magistad 1925).

stands in Ontario and Quebec indicated very high levels of water-extractable aluminum (for the forest floor mean ± SD was 85 ± 54 $\mu g \cdot g^{-1}$, range = 11-257 $\mu g \cdot g^{-1}$; for the mineral soils mean ± SD was 18 ± 18 $\mu g \cdot g^{-1}$, range = 2-92 $\mu g \cdot g^{-1}$ (Hutchinson and Bozic 1985)). These aluminum concentrations are sufficient to be toxic to nontolerant plant species. In another study that was done in the vicinity of a large smelter near Sudbury, Ontario, acidic surface soils within 2 km of the smelter had 51-99 $\mu g \cdot g^{-1}$ of water-extractable aluminum; these concentrations were toxic to several plant species in bioassays (Whitby and Hutchinson 1974). Aluminum was inhibitory to the root growth of several crop species at levels as low as 2 $\mu g \cdot mL^{-1}$ in solution.

It is well known that liming of soils to raise the bulk pH reduces the solubility of aluminum, and therefore its toxicity to plants, although this apparently simple remedy can be complicated by difficulties in delivering lime to acidic subsoils (e.g., Conner 1921; Evans and Kamprath 1970; Helyar and Anderson 1971; Foy 1974; Simpson *et al*. 1977; Ritchey *et al*. 1980, 1982; Haynes and Ludecke 1981; Bouton *et al*. 1982; Haynes 1984; Pavan *et al*. 1984). For example, Foy *et al*. (1965) added various quantities of $CaCO_3$ to an acidic (pH 4.1) soil, and found that increasing the pH to 5.5 decreased the extractable aluminum concentrations from 5.8 to 0.4 $meq \cdot (100\ g)^{-1}$, and increased the yield of barley (*Hordeum vulgare*) by a factor of 17.5 (Table 4-4). In another experiment, Haynes and Ludecke (1981) limed an acidic (pH 4.0) silt loam to a pH of 5.6, which decreased the exchangeable aluminum from 11.7 to 0.6 $meq \cdot (100\ g)^{-1}$. There are many other similar data in the literature. However, it should be noted that aluminum toxicity has also been demonstrated at relatively high pH; it occurs as a soluble aluminum hydroxide ($Al(OH)_4^-$) under these conditions (e.g., Magistad 1925; Rees and Sidrak 1956, 1961; Jones 1961; Farina *et al*. 1980a).

Conversely, agricultural or forestry practices that increase soil acidity will also increase the concentration of ionic aluminum and thus plant toxicity. Of special importance in this respect is the use of certain nitrogen fertilizers, such as ammonium nitrate, ammonium sulfate, and urea, which produce acidity via nitrification (Abruma *et al*. 1958; Pearson *et al*. 1962; Wolcott *et al*. 1965; Pierre *et al*. 1971; Russell 1973; Foy 1974; Awad *et al*. 1976; Hausenbuiller 1978; Otchere-Boateng and Ballard 1981). For example, Otchere-Boateng and Ballard (1981) examined the effect of urea fertilization and subsequent incubation of soil columns collected from a Douglas fir (*Pseudotsuga menziesii*) plantation on the leaching of aluminum. In columns in which Douglas fir seedlings were growing, the average (n=3) cumulative aluminum leachage increased 7.4-fold in columns fertilized at 448 $kg \cdot ha^{-1}$, compared with unfertilized columns. The increase in columns planted with western hemlock (*Tsuga heterophylla*) was 33-fold. The increased leaching of aluminum was attributed to a decrease in soil pH from an initial pH 5.5 to 3.9 at the end of the experiment, and also to the formation of mobile organic-aluminum complexes in the fertilized columns.

Although it is generally accepted that soil acidity affects the solubility and toxicity of aluminum, it has also been well demonstrated that

Table 4-4. Effect of liming on soil pH, KCl-extractable aluminum, and relative yield of barley (modified from Foy et al. 1965).

$CaCO_3$ added ($\mu g \cdot g^{-1}$)	Soil pH	Extractable aluminum ($meq \cdot (100\ g)^{-1}$)	Relative yield of barley
0	4.1	5.8	1.0
375	4.3	4.8	3.1
750	4.5	4.3	9.4
1500	4.8	2.8	14.8
3000	5.5	0.4	17.5

acidic soils of the same pH can have different concentrations of plant-available aluminum, and that they can be differentially toxic (e.g., Welch and Nelson 1950; Adams and Lund 1966; Richburg and Adams 1970; Foy 1974; Foy and Fleming 1978). Therefore, soil characteristics as well as bulk pH must be important in determining aluminum availability.

Soil organic matter is one such characteristic that has been shown to be negatively associated with aluminum availability (Pierre et al. 1932; Welch and Nelson 1950; Schnitzer and Skinner 1963; Clark and Nichol 1966; Pionke and Corey 1967; Evans and Kamprath 1970; Foy 1974; Thomas 1975; Ng Kee Kwong and Huang 1977; Holtzclaw et al. 1978; Bloom et al. 1979; Otchere-Boateng and Ballard 1981). This detoxification effect accrues from the formation of aluminum-organic matter complexes of relatively low solubilities, or to detoxification of Al^{3+} via chelation (Schnitzer and Skinner 1963). Organic aluminum is particularly important in the forest floor and surface mineral soils of natural plant communities. In a conifer podsol in Sweden, for example, organic aluminum constituted 94% of total aluminum in the organic-rich soil depth between 0 and 5 cm, whereas over 0-55 cm it averaged only 14% (Ulrich 1983). Bloom et al. (1979) found that the addition of organic matter (leaf humus) to an acidic (pH 4.0) soil decreased the concentration of Al^{3+}.

Another important soil factor that partly determines the availability of aluminum is phosphate. Under acidic conditions, phosphate combines with Al^{3+} to form $AlPO_4$, an insoluble mineral. This partly accounts for the decreased toxicity of acidic soils that have been fertilized with phosphate fertilizer (e.g., Conner 1916; Hartwell and Pember 1918; Mirasol 1921; Blair and Prince 1923; Pierre and Stuart 1933; Foy 1974; Awad et al. 1976; Bache and Crooke 1981; Haynes and Ludecke 1981; Haynes 1984). Other factors that have been shown to reduce aluminum toxicity in acidic soils include total ionic strength of the soil solution (Foy 1974; Misra et al. 1974; Pavan and Bingham 1982); calcium (Foy et al. 1969b; Lund 1970; Foy 1974; Simpson et al. 1977); and sulfate adsorption capacity (Abrahamsen and Stuanes 1980; Johnson 1980; Johnson and Cole 1980; Seip 1980; Johnson and Todd 1983). The first two factors act mainly via cation competition effects (for major soil cations, the replacement series at cation-exchange sites is $H^+ < NH_4^+ = K^+ < Ca^{2+} < Mg^{2+} < Al^{3+}$; Armson 1977), whereas the reduced mobility of anionic sulfate via adsorption implies less movement of associated cations (such as Al^{3+}), in accordance with the principle of conservation of electrochemical neutrality of ionic solutions.

4.4 ALUMINUM AND SOIL ACIDITY

Soil acidity results from the accumulations of soluble inorganic and organic acids at a rate faster than they can be neutralized or removed by leaching. Ionization of these acids produces free H^+ in the soil solution. Exchangeable H^+ also contributes to acidity. In addition, in strongly acidic soils (below pH 5.5), exchangeable aluminum can contribute to acidity through the ionization and hydrolysis of Al^{3+} (after Hausenbuiller 1978):

$$Al^{3+} + H_2O \rightleftharpoons AlOH^{2+} + H^+ \qquad [4\text{-}1]$$

The $AlOH^{2+}$ can also hydrolyze to produce $Al(OH)_2^+ + H^+$, but the $Al(OH)_2^+$ is present in low concentrations in acidic soil so that it normally contributes little to the total acidity.

Soils are usually strongly buffered, in comparison with fresh waters. However, different buffering systems come into play at particular pH ranges. $CaCO_3$ is important in soils with pH greater than 8 to 6.2; silicate buffers from pH 6.2 to 5.0; cation-exchange capacity (CEC) buffers from pH 5.0 to 4.2; aluminum buffers from pH 4.2 to 2.8; iron buffers from pH 3.8 to 2.4; and humic substances buffer from ca. pH 6 to 3 (Seip and Freedman 1978; Hausenbuiller 1978; Ulrich 1983).

Al^{3+} is the most toxic ionic form of aluminum in acidic soils, and below about pH 4 it can reach sufficiently high concentration in the soil solution to make it the most important edaphic factor limiting plant growth (Ulrich 1983; see also Chapter 1 for a more complete discussion of the relationship between pH and aluminum speciation). However, as will be discussed later, the tolerance of plant species or varieties to Al^{3+} varies greatly, and this can be a very important factor in the structuring of plant communities where soils are acidic. Furthermore, in very acidic soils (pH less than ca. 5), Al^{3+} and other toxic metal ions dominate the soil CEC, with the sum of $H^+ + Mn^{2+} + Al^{3+} + Fe^{3+}$ generally accounting for more than 90% of the CEC, whereas $Ca^{2+} + Mg^{2+}$ (which dominate the CEC in most circumneutral soils) account for less than 5-10% (Ulrich 1983).

Fox (1979) studied two acidic silt loam soils (pH 4.65 and 4.75, respectively) and found concentrations of exchangeable aluminum of 2.5 and 1.3 $meq \cdot (100\ g)^{-1}$, and aluminum CEC saturation percentages of 52 and 26%, respectively. Similarly, Pavan et al. (1982) studied six acidic soils (pH range of 4.0 to 4.3) from northern Brazil, and found concentrations of exchangeable aluminum that ranged from 0.6 to 4.1 $meq \cdot (100\ g)^{-1}$, and aluminum CEC saturation percentages that ranged from 37 to 79%. Similar data are in Lopes and Cox (1977), Mollitor and Raynal (1982), and Krug and Isaacson (1984); see also Reuss (1983) for a more general discussion of this problem.

4.5 ALUMINUM AND ACIDIC DEPOSITION

Concern has emerged during the past several decades regarding the ecological implications of the deposition of acidifying substances from the atmosphere to terrestrial and freshwater ecosystems. As is thoroughly discussed in other chapters of this report (particularly Chapter 3), aluminum has been identified as a critical factor influencing the toxicity of acidic fresh waters to biota. The likely source of much of this aluminum is the mineral soil of the terrestrial part of the watershed. Thus, aluminum could be considered an important, indeed possibly the most important, biogeochemical linkage between the terrestrial watershed and the acid/aluminum-susceptible biota of surface waters (e.g., Cronan and Scofield 1979; Norton et al. 1980).

Several recent studies have indicated that experimental acid loadings to forest soils will result in increased aluminum concentrations in the soil solution, and greater fluxes from lysimeters. Abrahamsen (1983) presented results of field experiments in a spruce (Picea abies) forest, where plots were irrigated with water ranging in pH from 2 to 6. The maximum average concentration (over 1976-1979) of aluminum in soil water collected with tension lysimeters from the upper B horizon was 0.32 $mg \cdot L^{-1}$ at an irrigation water pH of 6, 0.62 $mg \cdot L^{-1}$ at pH 4, 2.2 $mg \cdot L^{-1}$ at pH 3, and 34.8 $mg \cdot L^{-1}$ at pH 2. However, even at the most extreme experimental conditions (i.e., pH 2), there were no effects on tree growth, although the limitations of a 4-year study must be recognized.

In another experiment, Nilsson et al. (1983) irrigated intact soil (sandy podsol) columns, including the forest floor and ground vegetation, with acidic solutions (equivalent to ca. 33 kg H_2SO_4-$S \cdot ha^{-1} \cdot a^{-1}$, a rate that was close to ambient conditions). At the end of a 6-year experimental period, soil analysis indicated a moderate increase in exchangeable aluminum, with a total (mean ± SD) of 356 ± 45 $meq \cdot L^{-1}$ in the mineral horizons of the soils treated with sulfuric acid, compared with 312 ± 57 $meq \cdot L^{-1}$ in the controls. Nilsson et al. (1983) thought that the increase in exchangeable aluminum was derived from the solubilization of aluminum sesquioxides.

Krug and Isaacson (1984) treated a sandy loam with an acidic (pH 3.0) percolate and found increased aluminum concentrations compared with controls. The concentrations of aluminum in the 01 horizon (litter plus duff, 11-6 cm) increased from 4 $\mu eq \cdot cm^{-3}$ in the control to 15 $\mu eq \cdot cm^{-3}$ in the acid-treated soils, whereas in the Oe (humus, 6-0 cm) it was unchanged (20 and 18 $\mu eq \cdot cm^{-3}$, respectively), and in the Bh (surface mineral soils, 0-7 cm) it increased from 5 to 22 $\mu eq \cdot cm^{-3}$. These increases of aluminum in the 01 and Bh horizons were likely related to increases in their acidity as a result of the pH 3 irrigations; the pH decreased from 4.3 to 3.5 in the 01, and from 4.4 to 3.7 in the Bh, whereas in the unaffected Oe the pH decrease was more moderate, from 3.6 to 3.3.

In another acid irrigation experiment, Johnson and Todd (1983) treated an initially acidic (pH 4.6-5.0) hardwood forest soil with pH 3 waters at rates of H^+ loading that were equivalent to 2 and 10 times the ambient rates. In a preliminary report, they found no changes in exchangeable aluminum after 1 year.

In an experiment related to the dry deposition of acidifying substances, Lee et al. (1982) fumigated soils with SO_2 in open-top field chambers (soil acidity is generated when the dry-deposited SO_2 is oxidized to sulfuric acid, largely by chemoautotrophic bacteria). At the highest SO_2 dose (0.48 ppm SO_2 for a total of 275 h), the soil pH decreased from 5.8 to 4.9. Exchangeable aluminum concentrations increased markedly below pH 5.5 from 0.01 to 0.40 $meq \cdot (100\ g)^{-1}$, whereas aluminum saturation of the cation-exchange capacity increased from 0.45 to 6.5%.

Wet and dry deposition of acidifying substances and other air pollutants (e.g., ozone) have been linked to forest decline in western Europe and the northeastern United States. Damage has developed very rapidly in West Germany, with some degree of injury affecting an estimated 3% of the country's forested area in 1981, 8% in 1982, 34% in 1983, and more than 50% in 1984 (Anonymous 1984; Hileman 1984). Of the 34% of the German forests that were reported as injured in 1983, 2.5% were classified as severely injured, 25% as moderately injured, and 72.5% as slightly injured. The needles and even shoots, although still green, were prematurely shed from the trees. The ends of the branches lost needles last, and the dieback spread up the tree. Needles were often yellow, and analyses showed them to be magnesium-deficient. The damage involved a variety of tree species and was most severe at high altitudes where fogs are common. Forests in West Germany, Austria, Poland, Switzerland, Czechoslovakia, and southern Sweden have been affected.

The forest damage seemed to have been caused or triggered by drought, since the onset of the German forest decline was first noticed immediately after 2 years of severe drought in 1975 and 1976. Acidic rain may be a factor, but the damage occurred on many soil types, including some that are calcareous. The consensus is that regional air pollution problems are a major direct or indirect cause. Damage has been variously ascribed to oxidants (especially ozone), aluminum toxicity in soils (presumably acidifed in part by atmospheric deposition, plus enhanced acid generation by the oxidation of chemically reduced sulfur, ammonium, and other compounds during the drought years), SO_2, NO_x, and other gaseous mixtures, as well as to other edaphic factors (including plant pathogens), or to combinations of some or all of these. Interestingly, arboreal lichens, which are frequently quite sensitive to air pollution, flourish on the dead trees, possibly because of enhanced light or nutrient availability (Cowling 1983; Anonymous 1984; Linzon 1985).

An aluminum toxicity hypothesis was first espoused by Ulrich *et al.* (1980), who concluded: "Aluminum concentrations of 1 to 2 mg $Al \cdot L^{-1}$, as now occur continuously, should therefore seriously damage root systems of the trees especially in periods (seasons, years) where nitrification is favoured." They based these conclusions partly on evidence that aluminum concentrations in the soil solution of a beech (*Fagus sylvatica*) forest in West Germany had increased recently, from 360 $keq \cdot ha^{-1}$ in 1966, to 347 $keq \cdot ha^{-1}$ in 1973, and to 429 $keq \cdot ha^{-1}$ in 1979; these increases were accompanied by effects on roots characteristic of aluminum toxicity. However, it should be noted that the sampling was not very intensive in these studies, with only two replicates in 1966, four in 1973, and three in 1979. Overall, it appears that more field evidence is required before aluminum toxicity *per se* can be accepted as a causal agent in recent forest declines in areas receiving acidic deposition. This is especially true in view of data that suggest substantial tolerance to plant-available aluminum, by tree species that occur in naturally acidic soils (e.g., Humphrys and Truman 1964; McCormick and Steiner 1978; Ogner and Teigen 1980; Steiner *et al*. 1980; Rally 1983).

4.6 ALUMINUM CONCENTRATIONS IN PLANTS

The concentration of aluminum in plants varies greatly, from less than 1 $\mu g \cdot g^{-1}$ (dry weight) to several thousand micrograms per gram (Table 4-1). In part, this great range is because of the fact that some plant taxa, which are commonly found in acidic habitats, are hyperaccumulators of aluminum (Table 4-5). Hyperaccumulators are particularly frequent in the Diapensiaceae, Ericaceae, Lycopodiaceae, Melastomaceae, Symplocaceae, and Theaceae, among others (Hutchinson 1943, 1945; Lopes and Cox 1977; Bowen 1979). For example, Haridasan (1982) reported on a biogeochemical survey of 30 plant species from an acidic, oligotrophic red latosol in central Brazil. He found that 8 species (27%) were aluminum accumulators, with 4300-14 000 $\mu g \cdot g^{-1}$ (dry weight) in their foliage; the remaining 22 species contained 120-610 $\mu g \cdot g^{-1}$.

Plant aluminum concentrations tend to correlate with measures of aluminum availability in soils, although the most useful availability index may vary between soils or plant genotypes (e.g., Hackett 1965; Jones and Fox 1978; Fox 1979; Farina *et al*. 1980b; Mugwira 1980; Pavan *et al*. 1982). A number of edaphic factors can influence the availability of soil aluminum, and hence its concentration in plant tissues. These factors include bulk pH, phosphorus, and calcium levels. For example, Awad *et al*. (1976) investigated the influences of soil pH and phosphorus availability on the aluminum concentration in kikuyu grass (*Pennisetum clandestinium*), and found relatively high concentrations at low soil pH and low availability of phosphorus (Table 4-6).

In many plant species, higher concentrations of aluminum tend to occur in below-ground tissues than in above-ground tissues (this is especially true if bulk tissue samples of woody species are considered, but the trend also occurs if only foliage is considered) (Hutchinson 1943, 1945; Rasmussen 1968; Bartuska and Ungar 1980; Mathan 1980; Horst *et al*. 1983). For example, Bartuska and Ungar (1980) examined the compartmentalization of aluminum in birch (*Betula nigra*) and found 212 ± 19 $\mu g \cdot g^{-1}$ (mean ± SD) in foliage, 104 ± 25 $\mu g \cdot g^{-1}$ in woody above-ground tissues, and 3340 ± 950 $\mu g \cdot g^{-1}$ in roots. This pattern, however, does not always hold. The highest concentrations in tea (*Camellia sinensis*) occur in old leaves (Matsumoto *et al*. 1976a, b; Memon *et al*. 1981).

Table 4-5. Selected examples of aluminum hyperaccumulators.

Scientific name	Common name	Aluminum concentration in foliage ($\mu g \cdot g^{-1}$ (dry weight))	Reference
Camellia sinensis	Tea	30 700	Matsumoto *et al*. 1976a, b
Polytrichum juniperinum	Haircap moss	5 500	Hutchinson 1943
Fontinalis antipyretica	Aquatic moss	700	Hutchinson 1943
Lycopodium spp.	Clubmoss	≤ 26 500	Hutchinson 1943
Equisetum arvense	Horsetail	10 800	Hutchinson 1943
Hydrangea macrophylla	Hydrangea	13 000	Hutchinson 1943
Vochysia thrysoidea	-	14 100	Haridasan 1982
Qualea multiflora	-	11 500	Haridasan 1982
Palicourea rigida	-	9 900	Haridasan 1982

Table 4-6. The influence of soil pH and phosphorus fertilization on the aluminum concentrations in the above-ground tissues of *Pennisetum clandestinium*, an Australian pasture grass (after Awad *et al*. 1976).

	Aluminum concentration ($\mu g \cdot g^{-1}$ (dry weight))		
Soil pH	22 $kg \cdot ha^{-1}$ P	225 $kg \cdot ha^{-1}$ P	450 $kg \cdot ha^{-1}$ P
4.1	442	267	183
4.2	365	145	112
4.4	142	100	118
4.8	50	67	83
5.4	42	60	65
6.2	40	40	50

There have been several studies of aluminum compartmentalization within plant tissues. In tea leaves, aluminum was concentrated in the cell walls of the adaxial epidermis and pallisade parenchyma, especially in old leaves (Memon *et al*. 1981). Other studies have looked at the distribution of aluminum in roots. Both Rasmussen (1968) and Mathan (1980) examined maize (*Zea mays*), and found high concentrations on the surface of the root epithelial cells, with the highest concentrations at the root cap. Both authors postulated a co-precipitation of insoluble aluminum phosphate (the localization of phosphorus was "exactly the same" as that of aluminum; Rasmussen 1968). The root apex was also identified as critical in a vetch (*Vigna unguiculata*; Horst *et al*. 1983), sweet pea (*Pisum sativum*; Matsumoto *et al*. 1976c; Matsumoto and Mormura 1980), and cotton (*Gossypium hirsutum*; Naidoo *et al*. 1978). Matsumoto *et al*. (1976c) and Matsumoto and Mormura (1980) found particularly high concentrations of aluminum in root cell walls and nucleic acids of sweet pea, as did Naidoo *et al*. (1978) in the nucleus of cotton, and McLean and Gilbert (1927) in the nuclei of several crop species. The evidence of Matsumoto and Mormura (1980) strongly suggested that aluminum complexes with the phosphorus in DNA, and causes chromosomes to stick together rather than separate during cell division. Naidoo *et al*. (1978) also found an aluminum-phosphorus co-precipitate in the outer cells of the root cap of cotton. Interestingly, Wallihan (1948) rather emphatically refuted the aluminum phosphate co-precipitation hypothesis (the evidence up to that time is reviewed in Hutchinson 1943, 1945). However, he based his conclusions on relatively weak evidence concerning phosphorus and aluminum leakage from roots immersed in weak (0.001 N) sulfuric acid solutions; the leakage should not have occurred if (all of) the phosphorus and aluminum were present as aluminum phosphate, which would be insoluble under such conditions. However, he did not consider that other, more soluble forms of these elements might also be present.

4.7 EFFECTS OF ALUMINUM ON PLANTS

Aluminum is not generally essential for plant growth; most species grown in nutrient culture do not respond in terms of productivity to the presence of small available quantities of aluminum (Pratt 1966; Foy 1974; Foy *et al*. 1978; Bowen 1979). However, some species or varieties that grow on aluminum-rich acidic soils do have enhanced productivity under controlled conditions in the presence of small quantities of aluminum. This response has been demonstrated with pea (*Pisum sativum*) and millet (*Panicum milleaceum*) (Sommer 1926); tea (*Camellia sinensis*) (Hutchinson 1943, 1945; Matsumoto *et al*. 1976a, b); hairgrass (*Deschampsia flexuosa*) (Hackett 1962, 1965, 1967); alfalfa (*Medicago sativa*) and red clover (*Trifolium pratense*) (MacLeod and Jackson 1965); cranberry (*Vaccinium macrocarpon*) (Medappa and Dana 1970); *Eucalyptus* (Mullette 1975); and maize (*Zea mays*) (Clark 1977).

The symptoms of aluminum toxicity in plants are not usually diagnostic, because they may resemble the symptomatology associated with other metals or with phosphorus deficiency (Pratt 1966; Foy 1974; Foy *et al*. 1978). Roots are usually affected first. The overall appearance of the root system has been termed "coralloid"; initially root elongation is inhibited, followed by dwarfing, stuntedness, a brownish appearance, and a lack of fine branching of the roots. Such roots are very inefficient in the absorption of water, as a result of low surface area and poor exploitation of subsurface soil horizons. This leads to reduced rates of transpiration and impaired uptake of many essential nutrients. In addition, the emerging radicles of seedlings may lose their positive geotrophic response. Symptoms in above-ground tissues include an overall stunting and decreased yield, small dark green leaves, late maturity, purple-tinged coloration of various tissues, and yellowing or necrosis of leaf tips (Hartwell and Pember 1918; McLean and Gilbert 1927, 1928; Hutchinson 1943, 1945; Pratt 1968; Fleming and Foy 1968; Clarkson 1969; Reid *et al*. 1971; Foy 1974; Moore 1974; Foy *et al*. 1978; Foy and Fleming 1978; Wallace and Anderson 1984).

The various physiological effects of aluminum toxicity are extensively reviewed in the above references. In general, the effects include interference with cell division (especially in root tip meristems), fixation of phosphorus in less soluble forms in roots, decreases in root respiration, aluminum accumulation in nuclei and inhibition of DNA synthesis in roots, interference wth certain enzyme systems, decreases in transpiration, and interference with ion uptake (especially Ca and P) (Foy *et al*. 1978; Foy and Fleming 1978; Horst *et al*. 1983; Wallace and Anderson 1984).

It is impossible to generalize the toxic aluminum threshold required to achieve these various effects in plants, because of great genetic differences in susceptibility. These differences are apparent both between species and between varieties or ecotypes of particular species. Toxic thresholds in foliage for several species include: greater than 90 $\mu g \cdot g^{-1}$ in the grass *Pennisetum clandestinium* (Awad *et al*. 1976); greater than 300 $\mu g \cdot g^{-1}$ in rice (*Oryza sativa*; Tanaka and Navasero 1966); and greater than 100-150 $\mu g \cdot g^{-1}$ in the clover *Trifolium subterraneum* (Bouma *et al*. 1981; however, Munns (1965) found a greater than 400 $\mu g \cdot g^{-1}$ toxic threshold in this species). In some other species, plant tissue analysis has not been useful in predicting toxic effects (e.g., *Medicago sativa*; Bouma *et al*. 1981). To some extent, toxic thresholds can be moderated by high soil and/or tissue levels of calcium (e.g., Awad *et al*. 1976; Foy *et al*. 1969b; Foy and Fleming 1978; Huett and Menary 1980; Aniol 1983) or phosphorus (e.g., Jones and Fox 1978; Blamey *et al*. 1983).

4.8 ALUMINUM TOLERANCE IN PLANTS

Plant species and varieties/ecotypes vary greatly in their susceptibility to available aluminum in soils or nutrient solutions. A great deal of research has been done in this field, especially in agronomy, in order to identify species or varieties that might be appropriate for cultivation on sites with large quantities of plant-available aluminum. Recent reviews of this field are by Foy (1974), Foy *et al*. (1978), and Duvick *et al*. (1981).

One early study of interspecific differences in aluminum tolerance was reported by McLean and Gilbert (1927), who surveyed 12 crop species in solution culture. They used an ingenious split experimental design; the plants were grown for one-half of each week in a complete nutrient solution, but lacking aluminum, and the other half in solutions containing aluminum at various concentrations, but lacking phosphate. This design eliminated problems of aluminum detoxification via its precipitation as insoluble aluminum phosphate. They divided the responses into three arbitrary categories from sensitive to resistant species. Sensitive species showed reduced growth at 2 mg·L^{-1} Al in solution; included in this category were lettuce (*Lactuca sativa*), beets (*Beta vulgaris*), timothy (*Phleum pratense*), and barley (*Hordeum vulgare*). Moderately sensitive species were depressed at less than 7 mg·L^{-1}, and included radish (*Raphanus sativa*), sorghum (*Sorghum vulgare*), cabbage (*Brassica oleracea*), oats (*Avena sativa*), and rye (*Secale cereale*). Resistant species were depressed at greater than 14 mg·L^{-1}, and included maize (*Zea mays*), turnips (*Brassica rapa*), and redtop (*Agrostis stolonifera*). The redtop was especially tolerant, showing no root injury and only slightly reduced yield even at 50 mg·L^{-1}.

In a study that examined interspecific tolerance in 10 tree species, McCormick and Steiner (1978) found that 8 species tolerated from 80 to 160 mg·L^{-1} total aluminum in nutrient solution (including *Alnus glutinosa*, *Betula alleghensis*, *B. papyrifera*, *B. populifolia*, *Pinus rigida*, *P. sylvestris*, *P. virginiana*, *Quercus rubra*, and *Q. palustris*), whereas only 2 (a *Populus* hybrid and *Eleagnus umbellata*) were sensitive, i.e., were intolerant of 10-40 mg·L^{-1} Al. Other studies that have examined the relative tolerances of plant species to aluminum include those by Stoklasa (1922), Gilbert and Pember (1935), Jones (1961), Clymo (1962), Clarkson (1966), Grime and Hodgson (1969), Kamprath (1970), Bartuska and Ungar (1980), and Kamburov (1980).

Much more work has been done on intraspecific variation in aluminum tolerance than on interspecific differences. The most intensively studied species has been wheat (*Triticum aestivum*). For example, Foy *et al.* (1974) surveyed 46 cultivars in a high-aluminum soil and found an 8-fold variation in the yield of tops, and a 12-fold variation in the yield of roots. Other studies that have examined varietal differences in aluminum tolerance in wheat include those by Foy *et al.* (1965, 1967a, 1973a), Kerridge and Kronstad (1968), Mesdag and Slootmaker (1969), Kerridge *et al.* (1971), Dodge and Hiatt (1972), Lafever *et al.* (1977), Polle *et al.* (1978), and Campbell and Lafever (1981).

Other crop species in which varieties have been investigated for differences in aluminum tolerance include rice (*Oryza sativa* - Howeler and Cadavid 1976; Nelson 1983), maize (*Zea mays* - Clark 1977; Rhue *et al.* 1978), cotton (*Gossypium hirsutum* - Foy *et al.* 1967b, 1969a), dwarf bean (*Phaseolus vulgaris* - Foy *et al.* 1972; Malavolta *et al.* 1981), sorghum (*Sorghum bicolor* - Duncan 1981; Furlani and Clark 1981; Malavolta *et al.* 1981), rye (*Secale cereale* - Mugwira *et al.* 1980), barley (*Hordeum vulgare* - Foy *et al.* 1967a; Reid *et al.* 1969), triticale (*Tritico secale* - Mugwira *et al.* 1980, 1981), potato (*Solanum tuberosum* - Lee 1971a, b), tomato (*Lycopersicum esculentum* - Foy *et al*. 1973b), and soybean (*Glycine max* - Armiger *et al*. 1968; Foy *et al*. 1969b; Sartain and Kamprath 1978; Hanson and Kamprath 1979). Several turf or pasture grasses have also been examined, including ryegrasses (*Lolium perenne* and *L. multiflorum* - Vose and Randall 1962), bluegrass (*Poa pratensis* - Murray and Foy 1978), and fescues (*Festuca rubra* and *F. arundinacea* - Murray and Foy 1978). There have been few studies of ecotypes of native, nonagronomic species; we are only aware of studies on hairgrass (*Deschampsia caespitosa* - Cox and Hutchinson 1980) and paper birch (*Betula papyrifera* - Steiner *et al*. 1980).

In the few cases where the genetics of varietal tolerance to aluminum have been investigated, it has been shown to be very important. Campbell and Lafever (1981) found relatively high coefficients of heritability of aluminum tolerance in wheat, 0.91 for female parents, and 0.57 for male parents. Rhue *et al*. (1978) determined that aluminum tolerance in maize was under the control of only a single gene locus. Interestingly, although aluminum and manganese are both generally mobilized in toxic ionic forms in acidic soils, plant tolerance to these ions has not been shown to be genetically linked in several species (wheat and rice: Foy *et al*. 1973a; Nelson 1983). On the other hand, Cox and Hutchinson (1980) showed co-tolerances between aluminum and several heavy metals in the grass *Deschampsia caespitosa* growing in acidic soils near a base metal smelter in Ontario.

Several studies have indicated that nontolerant varieties of plants tend to increase the acidity of water-culture nutrient media in which they are grown, whereas tolerant varieties either do not change the acidity, or decrease it. Such an effect has been demonstrated in wheat, maize, and barley (Foy *et al*. 1967a, 1974; Foy 1974; Clark 1977; Foy and Fleming 1978). However, the phenomenon is not universal, as it was not observed in snapbeans (Foy *et al*. 1972). In nature, increases in the acidity of the rhizosphere or the surrounding soil as a result of the metabolic activities of nontolerant varieties would increase the solubilization of aluminum and other metals, with subsequent toxic effects, whereas increases in pH would reduce the toxic effects.

Several studies have found that aluminum-sensitive varieties of plants have relatively high root surface cation-exchange capacities, in comparison with tolerant varieties (wheat, triticale, barley, ryegrasses - Vose and Randall 1962; Foy *et al*. 1967a; Mugwira and Elgawhary 1979). This could be related to the observation that sensitive varieties of some species tend to accumulate more aluminum in their roots than do tolerant varieties (wheat and barley - Foy *et al*. 1967a, 1973; Polle *et al*. 1978; however, see Clark (1977) for conflicting observations with maize).

In addition, reduced uptakes of calcium, magnesium, potassium, and phosphorus have variously been found in sensitive plant varieties (Foy *et al*. 1972; Malavolta *et al*. 1981; Aniol 1983). Nitrogen nutrition, including the ionic source of nitrogen, is also important (Foy 1974; Foy *et al*. 1978; Foy and Fleming 1978). In acidic soils, the ammonium ion is by far the most abundant form of inorganic nitrogen in the soil solution or on cation-exchange sites; nitrate formation is inhibited by the greatly reduced rates of bacterial nitrification (Russell 1973).

4.9 ALUMINUM AND MICROORGANISMS

Very few studies have been published on the effects of aluminum on microorganisms. Although it is well recognized that litter decomposition and other microbial processes are severely retarded in acidic soils or forest floors, frequently leading to accumulations of large quantities of partly humified organic matter, these effects are generally ascribed to the acidity itself (especially via effects on bacteria), rather than to aluminum toxicity to microorganisms (e.g., Russell 1973; Armson 1977). Even studies that have specifically addressed the influence of toxic metals on microbial processes (recently reviewed by Freedman and Hutchinson 1980) have not considered the possibility of aluminum toxicity.

Few studies have examined the effects of aluminum on fungi. Thompson and Moore (1981) examined two mycorrhizal species that were early successional invaders of acid coal strip mine spoils. One species showed reduced growth of cultures only at greater than 350 $\mu g \cdot mL^{-1}$ aluminum in the culture medium, whereas with the other species *ca*. 50% of the cultures grew at 150 $\mu g \cdot mL^{-1}$. Thus, these fungi are quite tolerant of high concentrations of aluminum in their growth media. In another study, Firestone *et al*. (1983) showed that aluminum at concentrations above *ca*. 13 $\mu g \cdot mL^{-1}$ could inhibit the respiration of hyphal mats of *Aspergillus flavus*. This effect was greatly reduced in the presence of fluoride, because of the formation of an insoluble Al-F complex.

Several studies have examined the effects of aluminum on *Rhizobium* species, and on their symbiotic nitrogen-fixing relationships with legumes. Considerable differences exist between different species and strains of *Rhizobium* with respect to aluminum tolerance (Keyser and Munns 1979; Munns *et al*. 1979; Hartell and Alexander 1983), but, in general, the legume symbiont appears to be more sensitive than *Rhizobium* (Carvalho *et al*. 1981a; Franco and Munns 1982; Hartell and Alexander 1983).

Nevertheless, several studies have demonstrated decreased growth of *Rhizobium* in the presence of high concentrations of aluminum (e.g., Wood *et al*. 1984), and also decreased nodulation (Carvalho *et al*. 1981a, 1982a; Wood *et al*. 1984). Other studies have shown either no effect or relatively moderate effects on *Rhizobium* growth (Carvalho *et al*. 1981; Hartell and Alexander 1983), on nitrogen fixation (Carvalho *et al*. 1982b), and on nodule growth (Franco and Munns 1982). In addition, several studies have shown an ameliorative effect of calcium on aluminum toxicity to *Rhizobium* (Keyser and Munns 1979; Franco and Munns 1982).

4.10 SUMMARY AND CONCLUSIONS

Aluminum is an element of considerable interest. Although it is very common in the earth's crust, it is normally present in biota in much lower concentrations and is toxic to most organisms at low available concentrations, i.e., at a few micrograms per millilitre of ionic aluminum in solution.

In terrestrial ecosystems, aluminum toxicity is usually associated with acidic soils. Problems of soil acidity have long been recognized by farmers, and they have dealt with them by liming their fields. However, at the beginning of the present century, the important role of aluminum in the toxicity of acidic soils was also recognized. Much research resulted from this, particularly by agricultural scientists studying plants and soils. In general, they investigated the availability of toxic aluminum under various soil chemical conditions, the susceptibility of agricultural plant species or varieties to aluminum, and the specifics of the plant physiological response. Interestingly, much of this agricultural work was unknown to ecologists working in natural ecosystems, with the notable exception of a specialized group of physiological plant ecologists who were studying the calcicole-calcifuge problem.

Recently, scientists studying the ecological effects of the deposition of acidifying substances from the atmosphere have become acutely aware of (i) the fact that both naturally acidic and anthropogenically acidified soils contain high concentrations of toxic aluminum ions; and (ii) the likelihood that these soils are the source of the aluminum ions that are toxic to the biota of acidic, oligotrophic surface waters. Thus, with respect to the general ecotoxicology of acidification, aluminum may well be the most important biogeochemical linkage between the terrestrial and aquatic parts of the watershed. These observations have stimulated a great deal of interest and the beginnings of research on the specifics of the role that aluminum plays in the ecological impacts of acidic deposition.

In terrestrial ecosystems, particularly forests, this work is only beginning; to date studies have been made of aluminum mobilization and leaching from soils as a result of experimental additions of acidic solutions, and a few assays of the susceptibility of tree species have been conducted. The preliminary conclusions of this work are encouraging. For example, although it has been demonstrated that aluminum can be experimentally mobilized by acidic solutions, the degree of this effect is only great if very acidic solutions are used (i.e., much more acidic and at higher loading rates than are generally observed in nature). In addition, most of the few tree species that have been assayed to date have shown a considerable degree of tolerance to available aluminum; this is not unexpected because these species have been naturally selected for aluminum tolerance over very long periods of time, as they occur in acidic soils with high levels of aluminum availability (for example, the pH range of most podsols is ca. 3.5-4.5, and there are other naturally acidic soil types).

It is much too soon, however, to come to firm conclusions as to the possible implications of acidic deposition for aluminum toxicity in natural terrestrial ecosystems - a great deal more information is required. In fact, so few data are now available concerning the biogeochemical and biological responses to aluminum in natural terrestrial ecosystems that almost any new studies on virtually any topic would be useful. However, we feel that there are particular needs for further research on (i) the mobilization of aluminum in acidic or acidified terrestrial ecosystems, and the subsequent transfer to groundwaters and surface waters; (ii) the toxicity of aluminum to the biota of terrestrial ecosystems, including both commercially valuable (agricultural crops and forests) and other plant species, and soil animals; and (iii) the effects of available aluminum on soil microorganisms and the processes that they carry out, including litter decomposition and nutrient cycling (particularly nitrogen and phosphorus cycling).

5.0 ALUMINUM IN HUMAN HEALTH

D.R. Crapper McLachlan and B.J. Farnell

Department of Physiology
University of Toronto
Toronto, Ontario M5S 1A8

5.1 INTRODUCTION

Recent studies on the toxicity of aluminum have implicated this common environmental element as a pathogenic factor in several human diseases. Although pulmonary disease induced by massive amounts of certain forms of aluminum has been recognized for 40 years, the subtle delayed metabolic effects have only recently been reported. Attention in the past 10 years has been directed towards the toxicity of aluminum to brain, bone, and blood. Table 5-1 summarizes the human diseases in which increased concentrations of aluminum have been encountered.

5.2 ALUMINUM INGESTION

Kehoe *et al*. (1940) determined that the average North American diet contained 36.4 $mg \cdot d^{-1}$ Al (see Chapter 6). Although more recent estimates of average daily intake are similar (Underwood 1977; 25 mg), individual intake varies greatly, depending on the consumption of certain foods, beverages, and drugs containing large quantities of aluminum. There are several common examples (see also Tables 6-1, 6-2, and 6-3 in Chapter 6). The tap water of many communities contains aluminum in high concentrations either naturally or as a result of the purification process where aluminum sulfate is added as a flocculant. Processed cheese contains up to 0.66% Al by weight. Aluminum salts are used in some preserving and pickling processes, and are common buffers in drugs. Buffered aspirin contains up to 50 mg Al per tablet. Many antacid tablets contain 50-100 mg. A typical over-the-counter liquid antacid advertised for "indigestion, gas, heartburn and acid stomach" contains about 2 g Al in the manufacturer's recommended daily dose.

5.3 ALUMINUM METABOLISM

5.3.1 ABSORPTION, EXCRETION, TRANSPORT

With the exception of the lung, normal tissue levels of aluminum are low. Typical serum and tissue levels are in the range of 5 $\mu g \cdot L^{-1}$ serum and 1.5 $mg \cdot kg^{-}$ issue, respectively, in individuals who are not ingesting aluminum compounds regularly. Kaehny *et al*. (1977a) estimated the total body aluminum content in normal individuals at about 30 mg. This indicates that the skin, lung, and gastrointestinal tract are effective barriers to aluminum under conditions of average exposure. Kirsner (1943) examined aluminum hydroxide and aluminum phosphate in peptic ulcer treatment and described them as nonabsorbable compounds. However, Berlyne *et al*. (1972)

Table 5-1. Human conditions associated with elevated aluminum.

Disease	Reference
(a) Pulmonary fibrosis	Shaver and Riddell 1947
(b) Osteodystrophy	Hodsman _et_ _al_. 1982
(c) Anemia	Elliott _et_ _al_. 1978a
(d) Gastrointestinal disturbances	Hava and Hurwitz 1973
(e) Cardiotoxicity	Elliott _et_ _al_. 1978a
(f) Hepatotoxicity	Galle and Guidicelli 1982
(g) Postvaccine (DPT) granuloma	Savage 1973
(h) Cancer (bladder)	Theriault _et_ _al_. 1981; Dunkley 1982
(i) Neurological conditions	
1. Industrial exposure: Al ball mill worker	McLaughlin _et_ _al_. 1962
2. Alzheimer senile and presenile dementia	Crapper _et_ _al_. 1976; Trapp _et_ _al_. 1978; Perl and Brody 1979
3. Down syndrome with Alzheimer's disease	Crapper _et_ _al_. 1976
4. Guam and Kii peninsula (Japan) amyotrophic lateral sclerosis (spinal cord and brain) and Parkinson dementia with neurofibrillary degeneration	Yase _et_ _al_. 1974
5. Neurofibrillary degeneration adjacent to a hamartoma	Ebner _et_ _al_. 1975
6. Aged human brain	McDermott _et_ _al_. 1977
7. Dialysis encephalopathy	Alfrey _et_ _al_. 1976
8. Striatonigral syndrome - walls of blood vessels and parenchyma of putamen	Duckett and Galle 1976; Duckett _et_ _al_. 1976
9. Alcohol dementia with patchy demyelination and crystalline deposits	Lapresle _et_ _al_. 1975
10. Senile plaques of Alzheimer's disease	Duckett and Galle 1976; Duckett _et_ _al_. 1976

reported hyperaluminemia in humans from gastrointestinal absorption. This was observed in nondialyzed patients with chronic renal failure who were taking aluminum compounds (at 6 $g\cdot d^{-1}$ Al) to control hyperphosphatemia and/or hyperkalemia. A follow-up study using rats found significantly increased serum aluminum concentrations in both normal and uremic animals who were given aluminum in their drinking water. Berlyne et al. (1972) later described the effects of moderate doses of oral and parenteral aluminum salts in normal and uremic rats. Uremic rats had the highest serum aluminum concentrations and the greatest tissue loading. The aluminum poisoning was associated with periorbital bleeding, lethargy, anorexia, and death. Significant increases in the aluminum content of brain, liver, heart, bone, muscle, and serum were found. These authors proposed that aluminum deposition in the tissues may account for some features of the clinical syndrome of uremia in man.

Gastrointestinal absorption of aluminum by humans has since been studied by several groups. Clarkson et al. (1972) reported balance studies on eight patients with chronic renal failure who received 1.5-3.4 $g\cdot d^{-1}$ Al (oral aluminum hydroxide) over 20-30 d. Using neutron activation methods, a relatively insensitive detection method for trace amounts, these authors could not detect aluminum in unconcentrated urine and thus restricted their balance measurements to gastrointestinal elimination. Although they found no consistent changes in plasma aluminum concentrations averaged over the full control and experimental periods, they reported large positive balances in all subjects ranging from 100 to 480 $mg\cdot d^{-1}$ Al. The total absorption was 3-15 g per month. Cam et al. (1976) reported aluminum retention in both normal and uremic subjects taking 2.5 $g\cdot d^{-1}$ Al (oral aluminum hydroxide) for 23-28 d. These investigators were also unable to detect aluminum in the urine. Maximum aluminum absorption within their group of five normal patients was 97 $mg\cdot d^{-1}$ and 3 g per month, whereas the two renal patients absorbed an average of 173 $mg\cdot d^{-1}$ and 5 g per month. Cam et al. (1976) proposed an abnormality in the gut wall of patients with renal failure, leading to increased aluminum uptake.

Kaehny et al. (1977b) found increased aluminum concentrations in plasma and urine of normal subjects by employing sensitive atomic absorption techniques following a single oral dose of about 0.7 g Al contained in one of several different salts. The plasma aluminum concentration increased about 300% with aluminum hydroxide and about 200% with aluminum carbonate. Subjects taking aluminum phosphate (insoluble at acid pH) showed only a small increase in urinary excretion with an insignificant rise in plasma concentrations. Gorsky et al. (1979) used flameless atomic absorption methods to study aluminum balance in six patients with normal renal function, receiving 1-3 $g\cdot d^{-1}$ Al from a mixture of aluminum salts. These patients were studied over a period of 18-84 d during which time their average aluminum balance was always positive, ranging from 23 to 313 $mg\cdot d^{-1}$. Throughout one 6-d period one of the patients had an average positive aluminum balance of 1.8 $g\cdot d^{-1}$. During the period of intake the plasma aluminum concentration increased about threefold in four patients and remained within the normal range in two. Urinary aluminum increased about threefold in all six cases. In four subjects, the increased urinary excretion persisted beyond the period of aluminum ingestion, indicating partial excretion of the retained aluminum. However, maximum daily urinary aluminum excretion represented only 0.5% of the daily aluminum load absorbed, and there were indications that this urinary excretion returned to normal levels in a relatively short time. Verbeelen et al. (1980) found that 1 h after ingestion of 1 g Al (oral $Al(OH)_3$), the average serum aluminum concentration increased from 38 ± 7.5 to 51 ± 1 $\mu g \cdot L^{-1}$ in 12 healthy subjects.

Although the main route of elimination of ingested aluminum is the alimentary tract, considerable evidence is consistent with the view that some aluminum is absorbed and enters the circulation. The solubility of different $Al(OH)_3$ preparations varies considerably (Litman 1967), and the availability of free aluminum is 2 to 3 orders of magnitude higher at pH 4 than at pH 6.2 (Kaehny 1977b). Cam et al. (1976) suggested that gastrointestinal absorption of aluminum occurs in the acidic new environment of the stomach and duodenum. The precise mechanisms involved in this transport of aluminum are unknown. Mayor et al. (1977) found greatly increased absorption and retention of orally ingested aluminum in rats treated with parathyroid hormone (PTH). Whereas serum aluminum concentration was only slightly increased with PTH, concentrations in kidney, muscle, bone, whole brain, and brain gray matter were much higher than in rats given aluminum alone. Furthermore, in similar studies it was shown that continuation of the hyper-PTH state sustained the increased body content of aluminum after exposure stopped (Mayor et al. 1980). The withdrawal of PTH resulted in rapid exit of aluminum from brain independent of continued dietary aluminum. Studies using rat everted gut sac preparations indicated a direct effect of PTH on aluminum metabolism, resulting in decreased transport and increased tissue avidity for aluminum (Feinroth et al. 1980). These findings are consistent with the possibility that gastrointestinal absorption of aluminum may involve an active process, perhaps related to calcium transport.

Several investigators have reported that plasma aluminum is partitioned between ultrafilterable (non-protein-bound) and protein-bound fractions. Studies in normal man using ultrafiltration and flameless atomic absorption techniques found that at normal blood levels (40 ± 7 $\mu g \cdot L^{-1}$ Al), about half of the aluminum is plasma-bound to protein of greater than 8000 molecular weight and the remainder is non-protein-bound and ultrafilterable. Clearance studies in dogs have confirmed this (Kovalchik et al. 1978). Elliott et al. (1978b) concluded that in dialysis patients with plasma aluminum concentrations greater than 200 $\mu g \cdot L^{-1}$, 60-70% of the aluminum was bound to high-molecular-weight protein, 10-20% was bound to albumin, and 10-30% was ultrafilterable. Two studies using gel filtration chromatography found plasma aluminum bound to several protein fractions which included albumin and an unidentified large-molecular-weight fraction of about 70 000 to 90 000 daltons (King et al. 1979; Toda et al. 1980). Trapp (1983) used in vivo competition studies, gel filtration chromatography, and UV difference spectroscopy techniques to identify transferrin (molecular weight 76 000) and albumin as the main protein sites binding aluminum in blood. Aluminum ion is bound to at least one of the two specific iron-binding sites of serum transferrin. A unique property of the transferrins is the requirement of CO_2 for binding Fe^{3+}, and this property is maintained for the binding of Al^{3+} ion. Trapp (1983) calculated the serum-binding capacity for aluminum at 680 $mg \cdot L^{-1}$ assuming a K_a of 10^{-20} M for the reaction (K_a for Fe^{3+} is 10^2 M):

$$Al^{3+} + \text{apotransferrin} \rightarrow Al^{3+}\text{-transferrin} \qquad [5\text{-}1]$$

The equilibrium concentration of unbound aluminum would be about 10^{-12} M. It was suggested that very little free plasma aluminum exists and that all plasma aluminum in normal subjects is transferrin-bound. However, these calculations do not take into account the hydroxylation of aluminum ion in solution or to what extent this and other speciation of "free" aluminum affects the true unbound aluminum-transferrin binding equilibrium. In fact, the data (Trapp 1983) show that about 70% of the total bound aluminum is distributed equally between the albumin and transferrin fractions. Speciation of aluminum in solution is probably an important determinant of the ultrafilterable-bound compartmentalization in plasma. Karlik (1979) suggests that the ultrafilterability of aluminum may result from the presence of hydroxylated species at plasma pH. At pH 7, 80% of aluminum in solution can be found as neutral species and may easily pass glomerular or capillary membranes.

The precise mechanisms of aluminum handling by the kidney are unknown. Berlyne _et al_. (1972) noted that the clearance of aluminum was less than that for either urea or creatinine, and suggested that tubular reabsorption was involved. This observation can now be accounted for by decreased filtration of aluminum because of protein binding. The very low excretion rate found with normal low plasma aluminum concentrations is probably because of the strength of this protein binding. However, urinary excretion does increase with increased aluminum uptake. Kaehney _et al_. (1977a) observed that plasma protein binding of aluminum was apparently saturable. After such saturation urinary excretion would increase following an increase in unbound filterable aluminum. Presumably, such filterable unbound aluminum species have access to extracellular and intracellular compartments, allowing tissue accumulation during aluminum loading.

In conclusion, healthy mammals are well adapted to detoxify "natural" or low environmental levels of aluminum. The combination of low gastrointestinal absorption, plasma protein binding, and renal excretion of the free and filterable fraction prevents the accumulation of all but trace amounts of this potentially toxic metal. However, the ingestion of the antacid or phosphate-binding gels increases the aluminum burden by amounts that are exceedingly large when compared with the normal total body content. Other common drugs and certain food products also contain large amounts of aluminum. In all situations of chronic overexposure to aluminum from any sources, the potential effects of aluminum accumulation in tissues require consideration.

5.3.2 CYTOTOXICITY

Table 5-2 summarizes the known interactions of aluminum with nuclear, cytoplasmic, membrane, and body fluid constituents of living organisms. These interactions may, in part, account for the pathogenic properties of aluminum.

5.4 HUMAN DISEASES ASSOCIATED WITH ALUMINUM

5.4.1 PULMONARY DISEASES

Shaver and Riddell (1947) reported distinctive pulmonary fibrosis with emphysema in aluminum abrasive (carborundum) workers. Lung disease in workers exposed to finely powdered aluminum metal has also been documented (Mitchell 1959; Mitchell *et al*. 1961; Jordan 1961; McLaughlin *et al*. 1962). The material associated with these cases is finely flaked particulate material produced by stamping, and is used in paints, explosives, and pyrotechnical devices. Although various grades of aluminum flakes may be treated with mineral oil or stearin to prevent agglomerations, the epidemiology does not suggest that these additives affect the incidence or character of the resulting pulmonary fibrosis. A coarser variety of aluminum dust produced from molten metal, or by means other than stamping, appears to be much less dangerous, although radiological changes in the lungs may result from exposure. The clinical picture consists of dyspnea, pneumothorax, and variable sputum production. Some fatalities have resulted. The chest film and histopathology are typical of a nonnodular interstitial fibrosis. Airway obstruction, emphysema, and impaired alveolar-capillary gas diffusion are not prominent features. The absence of severe emphysema distinguishes, to some degree, the pulmonary fibrosis caused by aluminum dust from that considered typical of Shaver's disease. Silica content of the fumes responsible for the latter disease may be relevant to the dissimilarity. Prominent encephalopathic features accompanying a case of pulmonary fibrosis were described by McLaughlin *et al*. (1962). These were the first workers to recognize that aluminum accumulated in the brain.

5.4.2 OSTEODYSTROPHY

Aluminum has several effects upon bone metabolism, and bone is the one tissue in which aluminum toxicity is clearly implicated in human disease other than as part of the dialysis encephalopathy syndrome (DES). There are at least two types of aluminum-related bone diseases. Hypophosphatemic osteomalacia is an indirect effect of systemic aluminum exposure and is unrelated to DES. Osteomalacic renal osteodystrophy, which appears to be a direct manifestation of aluminum toxicity, is an important consideration in all cases of renal failure and in certain other circumstances involving aluminum exposure.

Table 5-2. Actions of aluminum at the cellular level.

Effects	Reference
(A) NUCLEAR EFFECTS	
1) Binds to DNA phosphate and bases	Karlik et al. 1980
2) Increases histone-DNA binding	Crapper McLachlan et al. 1983
3) Blocks initiation sites for RNA polymerase	Sarkander et al. 1983
4) Blocks RNA polymerase activity in vitro	
5) Blocks ADP ribosylation	Crapper McLachlan et al. 1983
6) Alters sister chromatid exchange	De Boni et al. 1980
7) Alters steroid-induced chromosome puffing	Sanderson et al. 1982
8) Inhibits corticosterone receptor binding to DNA	Sanderson et al. 1982
9) Decreases cell division and alters DNA synthesis	Gelfant 1963; Sampson et al. 1963
(B) CYTOPLASMIC EFFECTS	
1) Induces conformational changes in calmodulin Blocks calmodulin-dependent Ca/Mg-ATPase which is important in the extrusion of Ca^{2+} from cells	Siegal and Haug 1983 Siegal and Haug 1983
2) Reduces sugar phosphorylation	Rorison 1965
3) Decreases respiration	Foy 1974
4) Increases intracellular calcium content	Burnatowska=Hledin and Mayor 1982; Farnell et al. 1982
5) Inhibits hexokinase; stabilizes terminal phosphoryl group on ATP	Trapp 1980

Table 5-2 (Cont'd)

Effects	Reference
(C) MEMBRANE EFFECTS	
1) Alters physical properties of membrane lipids	Viestra and Haug 1978
2) Blocks high affinity uptake of GABA and glutamate from synaptosomes	Wong *et al*. 1981; Sturman *et al*. 1983
3) Blocks synaptosome uptake of neurotransmitter amines, choline, dopamine, and noradrenaline	Lai *et al*. 1978, 1980
4) Inhibits acetylcholinesterase	Miller and Levine 1974; Marquis and Lerrick 1982
5) Alters adenyl cyclase activity	Mansour *et al*. 1983
6) Enhances brain-specific lipid peroxidation	Ohtawa *et al*. 1983
7) Blocks uptake of calcium and acetylcholine binding	Hava and Hurwitz 1974
(D) BLOOD	
1) Alters activity of cholinesterase	Patockna 1971; Marquis 1983
2) Interacts with transferrin	Trapp 1983

In animal studies, Cox *et al.* (1931) produced bone loss with aluminum-induced phosphate depletion. Oral intake of aluminum containing antacids has been known to affect calcium and phosphate metabolism in humans since the work of Fauley *et al.* (1941) and Kirsner (1943) on the treatment of peptic ulcer. Aluminum doses of 1.5 $g \cdot d^{-1}$ over 4 d increased urinary calcium, decreased urinary phosphate, and increased fecal phosphate excretion. Subsequently $Al(OH)_3$ was thought to be useful in the prevention of recurrent phosphate-containing renal calculi (Shorr and Carter 1950). Bloom and Flinchum (1960) described osteomalacia with pseudofractures and bone pain resulting from long-term use of $Al(OH)_3$. Lotz *et al.* (1968) then described a syndrome of phosphate depletion with osteomalacia, which resulted from the intake of large amounts of aluminum-containing antacids. Although the associated hypercalcuria was attributed to increased intestinal calcium absorption, calcium kinetic studies suggest increased bone resorption during the aluminum ingestion. Spencer *et al.* (1982) confirmed the report by Lotz and co-workers of a negative calcium balance in patients taking low doses of aluminum-containing antacids while on a diet low in calcium (250 $mg \cdot d^{-1}$). These authors found no change in the gastrointestinal absorption of calcium and attributed the increased urinary calcium directly to increased bone resorption. The concurrent use of a diet providing 800 $mg \cdot d^{-1}$ Ca prevents the hypercalcuria caused by aluminum ingestion (Cam *et al.* 1976; Cooke *et al.* 1978; Spencer *et al.* 1982). Spencer *et al.* (1982) have suggested that the high calcium intake may reduce or counteract the antacid-induced bone resorption.

Phosphate is an important regulator of bone metabolism (Firschein 1969), and phosphate deprivation is known to stimulate bone reabsorption (Cuisinier-Gleizes *et al.* 1971). Most patients with chronic renal failure have hyperphosphatemia, and the osteomalacia induced by phosphate depletion occurs frequently as a rare end-stage complication. It is generally reversible following withdrawal of the aluminum-containing antacid, with the return of normal serum phosphorus (Dent and Winter 1974; Cooke *et al.* 1978; Insogna *et al.* 1980). This appears to be etiologically separate from the aluminum-induced osteomalacic component of renal osteodystrophy, which is associated with normal serum calcium and phosphate.

Approximately two-thirds of patients suffering from DES have bone disease characterized by the triad of progressive skeletal pain, proximal muscle weakness, and fracturing osteomalacia (Wing *et al.* 1980; Garcia-Bunuel *et al.* 1980). The bone histology in these patients is abnormal, usually pleomorphic, and is characterized by hyperosteoidosis, reduced osteoblastic activity, and a greatly decreased mineralization front (Drueke 1980). Platts *et al.* (1977) investigated the uneven geographical distribution of dialysis encephalopathy and spontaneous fractures in over 200 patients on home hemodialysis. They found that these complications were associated with the use of tap water that contained lower concentrations of calcium and fluoride, and higher concentrations of aluminum and manganese. Furthermore, higher aluminum and manganese contents were associated with the occurrence of multiple fractures. These authors did not attribute a causal role to aluminum specifically, but concluded that "some contaminant in the water used for dialysis was very probably responsible." Ward *et al.* (1978)

used tap water with high aluminum content in their dialysis centers and reported that osteomalacia was present in 70% of patients using nondeionized water, and in 15% of those using deionized water from the same source. They concluded that aluminum was a likely etiological agent. Several papers have since reviewed the evidence relating aluminum in bone to this osteodystrophy (Parkinson et al. 1979; Drueke 1980; Cochran et al. 1981). It is generally agreed that the occurrence and then disappearance of geographically clustered osteodystrophy, associated with dialysis encephalopathy, correlates in a highly significant manner with the aluminum content of water used to prepare the dialysate, and with its subsequent removal by deionization.

Renal osteodystrophy is more widespread than DES. Work by Hodsman et al. (1981) and others showed that sporadic cases of dialysis osteomalacia occur in dialysis centers having little or no experience with dialysis encephalopathy. Several reports from as early as 1971 indicated that bone aluminum is substantially elevated in uremic patients in general, particularly in those undergoing hemodialysis (Parsons et al. 1971; Ellis et al. 1979; Alfrey et al. 1979, 1980). Bone pain is a common symptom in chronic renal failure patients on long-term hemodialysis (Willis and Savory 1983), and histological bone disease is present in nearly all patients with renal failure. This renal osteodystrophy is actually a group of bone disorders that can be classified histomorphometrically. Hodsman et al. (1982) studied 59 patients with renal osteodystrophy and found pure osteomalacia in 23, osteitis fibrosa in 13, mixed lesions in 7, and mild lesions in 16. Bone aluminum exceeded normal values in all groups, but was significantly higher in patients with osteomalacic compounds than in those with other skeletal lesions. In the osteomalacic group there was also a strong correlation between bone aluminum concentration and the extent of unmineralized osteoid. All osteomalacia is characterized by a defect in mineralization of the organic matrix. Aluminum-related osteomalacia tends to be a severe progressive form with bone pain, fractures, deformity, and myopathy (Kerr 1981). It occurs despite the maintenance of normal plasma calcium, magnesium, and phosphate at concentrations that would not interfere with bone mineralization in healthy individuals (Varghese et al. 1973). Unlike classical osteomalacia it is unresponsive to treatment with vitamin D compounds, even though a normal hypercalcemic response is obtained.

Ellis et al. (1979) found an increase in bone aluminum in rats following intraperitoneal injection of aluminum chloride. This was associated with impaired mineralization in endochondrial cartilage and the development of osteomalacia. The bone pathology appeared after a latent period of about 8 weeks after beginning aluminum treatment, and persisted for up to 7 weeks following cessation of the injections. In a similar study, Robertson et al. (1983) found that chronic renal failure increases the severity of aluminum-induced osteomalacia. Furthermore, the double tetracycline label technique indicated that aluminum administration causes a reduction in the rate of both bone formation and bone resorption.

The role of parathyroid hormone (PTH) in renal osteodystrophy is controversial. Coburn et al. (1977) reported vitamin D-resistant osteomalacia in uremic patients with essentially normal iPTH levels. There was no evidence of phosphate depletion, and hypercalcemia developed rapidly with vitamin D therapy. Ellis et al. (1977) described similar patients. Cournot-Witmer et al. (1981) studied aluminum localization in the bone of two groups of hemodialyzed patients having osteomalacia or osteitis fibrosa. The osteomalacia group was resistant to vitamin D therapy and had no abnormalities in phosphate, calcium, vitamin D, or iPTH levels. Plasma aluminum was above normal in both groups, but significantly higher in the osteomalacia group. The osteitis fibrosa group had significantly increased plasma iPTH levels, and these authors suggested that this secondary hyperparathyroidism may in some way prevent the aluminum-induced mineralization defect.

The studies of Hodsman et al. (1981) and Cournot-Witmer et al. (1981) confirmed that a large majority of dialysis patients with associated osteomalacia have normal levels of PTH, well below the level of those with osteitis fibrosa. Kraut et al. (1983) reported a decreased PTH response to hypocalcemia in osteomalacic patients, and Felsenfeld et al. (1982) reported the development of osteomalacia in several dialysis patients following parathyroidectomy for osteitis fibrosa. Robertson et al. (1983) studied the role of chronic renal failure in an animal model of aluminum-induced osteomalacia. They found a decrease in amino terminal PTH in aluminum-treated osteomalacic rats, despite the presence of hypocalcemia. All of these results suggest that a relative PTH deficiency may be a contributing factor in the aluminum-induced osteomalacia.

Mayor et al. (1977) found a correlation between serum iPTH and serum aluminum in patients undergoing hemodialysis. However, Ellis et al. (1979), Alfrey et al. (1979), and Cournot-Witmer et al. (1979) did not find a relationship between increased bone aluminum and serum iPTH in uremic patients. Furthermore, compared with patients having other forms of renal osteodystrophy, those with osteomalacia have the highest levels of aluminum in serum (Cournot-Witmer et al. 1981) and bone (Hodsman et al. 1982). Both of these studies reported an inverse correlation between serum iPTH and the presence of aluminum-induced osteomalacia. Morrissey et al. (1983) found that at 0.5-2 mM, aluminum directly inhibited both the basal and isoproterenol-stimulated secretion of PTH from dispersed bovine parathyroid cells. They proposed that the accumulation of aluminum in parathyroid tissue may thus induce a decreased serum PTH.

Hodsman et al. (1982) suggested an evolutionary view of renal osteodystrophy where osteomalacia is preceded by osteitis fibrosa with an intermediate stage of mixed histopathology. This is a useful concept allowing us to hypothesize a sequence of events beginning with an aluminum-induced increase in PTH levels and the appearance of osteitis fibrosa. A subsequent decrease in serum PTH and the decreased PTH response to hypocalcemia may be the result of aluminum accumulation in the parathyroid gland. At this stage the PTH "protection" of bone from demineralization declines, the aluminum content of bone increases specifically at the mineralization front, and osteomalacia develops.

The localization of bone aluminum has been studied using histochemical staining, analytical ion microscopy, and electron-probe X-ray microanalysis (Buchanan *et al.* 1981; Cournot-Witmer *et al.* 1981; Robertson *et al.* 1983). Each of these studies indicated that aluminum is localized mainly at the interface between osteoid and calcified matrix of the osteomalacic bone in both aluminum-treated rats and in hemodialysis patients. This localization suggests that aluminum may somehow interfere directly with the normal mineralization process. In 1970, Bachra and van Harskamp found that 1 µM aluminum can precipitate calcium apatite from a calcification buffer, and Ellis *et al.* (1979) postulated that aluminum may interfere directly with phosphate metabolism at the mineralization front.

Cournot-Witmer *et al.* (1981) reported a reduction in the number of active bone cells in their dialysis patients with osteomalacia, and suggested that aluminum may have some effect on bone cells. Lieberherr *et al.* (1982) studied the *in vitro* effects of aluminum on bone phosphatases and found that it directly influences bone cell metabolism. Aluminum concentrations ranging from 0.03 nM to 1.5 µM induced a dose-dependent increase in acid and alkaline phosphatase activities. Concentrations of 3 µM or higher produced a significant decrease in the activity of both enzymes. These effects are modulated by the concentrations of calcium and phosphate in the incubation medium. The stimulation of bone phosphatase activity by PTH or 1,25-dihydroxy vitamin D is significantly inhibited by 1.5-6 µM Al. Interestingly, these concentrations are comparable to the circulating aluminum concentrations found in hemodialyzed patients (6 µM or 200 $\mu g \cdot L^{-1}$) and are similar to plasma values of aluminum in uremic patients. These results are consistent with the observations of normal or low plasma alkaline phosphatase in uremic patients with elevated plasma aluminum, and may account for the characteristic vitamin D resistance of this osteomalacia. Presumably the localization of aluminum along the mineralization front attains concentrations that are sufficient to cause destruction of bone cells.

Although the prevalence of osteomalacia resulting from oral aluminum therapy is unknown, Boyce *et al.* (1982) suggested that, in chronic renal failure, it may be more widespread than is yet recognized. In addition, the possibility that such toxicity may occur in the absence of renal failure is also a reasonable concern. Interestingly, some patients surviving on chronic total parenteral nutrition develop metabolic bone disease with bone pain and fractures after many months, when other signs of malnutrition are improving (Shike *et al.* 1980; Klein *et al.* 1980). Ott *et al.* (1983) examined bone biopsy specimens from 16 patients on total parenteral nutrition who had symptoms of bone disease and normal renal function. They reported stainable bone aluminum localized at the mineralization front in 14 out of 16 patients. Aluminum was associated with low bone formation similar to the osteomalacia found in aluminum-intoxicated patients on hemodialysis. The bone formation rate correlated inversely with the logarithm of bone aluminum content. Each of these 14 patients had been receiving a casein hydrolysate containing 2.3 $mg \cdot L^{-1}$ Al, and at the time of the study their PTH levels were either undetectable or in the lower range of normal.

In summary, it is clear that chronic aluminum exposure is toxic to bone regardless of the state of renal function. The precise factors regulating aluminum toxicity in bone are incompletely understood, and, in particular, the role of PTH demands clarification. In this regard, it is important at least to consider the potential for harm in any person who is exposed to even low amounts of aluminum with active bone disease from altered parathyroid function or from other causes.

5.4.3 ANEMIA

Elliott et al. (1978a) were the first to report a severe anemia preceding the encephalopathic and osteomalacic symptoms of DES. They described eight patients who had serum aluminum concentrations over 550 $\mu g \cdot L^{-1}$. Five of these patients had radiological and histological evidence of osteomalacia, and two had symptoms of bone or muscular pain. Six of the eight had neurological symptoms. All eight patients had decreasing hemoglobin concentrations in the 12 months preceding the onset of encephalopathic symptoms and/or the detection of high serum aluminum. During this period, the average hemoglobin concentration for the eight patients fell progressively from 9.1 to 5.4 $g \cdot dL^{-1}$. Several authors have since confirmed that this is a microcytic hypochromic anemia, different from the uncomplicated anemia of chronic renal failure which is a normocytic normochromic type. Although microcytic anemia in hemodialysis is generally attributed to iron deficiency, this disorder occurs despite normal serum ferritin and adequate supplementation with iron, folate, vitamin C, and pyridoxine (Elliott and MacDougall 1978; Short et al. 1980; O'Hare and Murnaghan 1982). In each of these studies, the hypochromic and microcytic character of the anemia was found to be reversible after deionization of the dialysate water. Touam et al. (1983) reported the same anemia in 10 chronic hemodialysis patients without DES who had plasma aluminum levels of 15.1 ± 3.1 μM. Ten nonanemic patients who were matched for age, extent of renal disease, dialysis treatment, and oral aluminum load had plasma aluminum levels of 1.43 ± 0.29 μM. Serum iron concentration did not differ between those two groups, and serum ferritin was within the normal range. The microcytosis was reversed following deionization of the dialysis water. These authors also found that parenteral aluminum administration to uremic rats led to microcytic hypochromic anemia comparable with that observed in aluminum-intoxicated hemodialysis patients. After 3 months of aluminum treatment these rats had plasma aluminum levels of 9.6 ± 1.1 μM (controls, 0.69 ± 0.11), with no changes in serum iron or tranferrin iron-binding capacity (Touam et al. 1983).

Although the etiology of this anemia is unknown, the induction of an iron deficiency state by aluminum seems to have been excluded. Touam et al. (1983) suggested that because aluminum accumulates in bone of hemodialysis patients, where it may lead to osteomalacia, it might directly interfere with erythropoiesis in the bone marrow. Furthermore, the microcytic hypochromic features of the anemia are consistent with a disturbance in hemoglobin synthesis. Huber and Frieden (1970) reported that 2-10 μM Al inhibits the in vitro activity of ferroxidase in both a competitive and noncompetitive manner with respect to the substrate Fe^{2+}. In addition, aluminum has been shown to interfere with d-aminolevulinic acid dehydrogenase, the second enzyme in the heme biosynthetic pathway (Meredith et al. 1979).

5.4.4 GASTROINTESTINAL TOXICITY

Gastrointestinal disturbances, including general malaise, anorexia, vomiting, and weight loss, have been described in several reports of DES. In normal man, the constipating effect of aluminum-containing antacids is well known.

Hurwitz and Sheehan (1971) and Hurwitz (1971) reported delayed gastric emptying and decreased gastrointestinal drug absorption in rats given oral antacids containing aluminum. The amount of gastric retention varied with different antacids, but was proportional to the amount of aluminum released. Hava and Hurwitz (1973) found that the addition of 0.5 mM $AlCl_3$ to the incubation medium of rat and human gastric muscle causes relaxation and a 31% decrease in the maximal contractile response to acetylcholine. In the rat preparation this was preceded by a brief aluminum-induced contraction. A similar inhibition of contractility was observed using isolated perfused rat stomachs. In each of these studies aluminum and lanthanum were found to have virtually identical effects. These observations hold true for the effects of lanthanum on other types of smooth muscle as well, including those of small and large intestine, uterus, and vascular tissues (Weiss and Goodman 1969; Goodman and Weiss 1971a, b). One may therefore accept that aluminum also affects smooth muscle contractility in several tissues. Considerable evidence suggests that aluminum directly inhibits smooth muscle contractility by an interference with calcium metabolism in the muscle cell.

The acute constipation that follows oral aluminum intake is most likely the result of contractility inhibition. It is not known whether the gastrointestinal symptoms associated with DES can also be attributed to aluminum. One would expect chronic aluminum overload to directly result in a disorder of gastrointestinal motility. The long-term effects of such a condition are unknown. It is noteworthy that of all the tissues analyzed by Flendrig et al. (1976), the aluminum content of pancreas and liver showed the greatest increases (66- and 39-fold, respectively) in DES. The symptoms of general malaise, anorexia, vomiting, and weight loss have been observed during and prior to the onset of frank encephalopathy. Elliott and MacDougall (1980) stated that although these are "nonspecific features" and difficult to quantify, it is not unreasonable to ascribe them to systemic aluminum intoxication.

5.4.5 CARDIOTOXICITY

Of 12 fatal DES cases reported by Elliott et al. (1978a), 4 suffered sudden cardiac death. These patients were young (ages 28, 29, 34, and 44) and had no recent history of hypertension or ischemic heart disease. A nonencephalopathic patient with a serum aluminum concentration of 600 $\mu g \cdot L^{-1}$ also died under similar circumstances. These cases were presented with acute pulmonary edema at times when they appeared to be in good fluid and electrolyte balance. The full details of these cases were not reported and we must assume that causes such as high output failure because of anemia were ruled out.

The myocardium utilizes magnesium-activated ATPase (Alpert and Gordon 1962; Katz 1970), and aluminum is known to inhibit this enzyme (Lai et al. 1980). Sudden myocardial deaths have been associated with depletion of myocardial magnesium (Seller 1971; Behr and Burton 1973), and Elliott et al. (1978a) proposed that the high aluminum levels in DES could thus exert a cardiotoxic effect.

5.4.6 HEPATOTOXICITY

Galle and Guidicelli (1982) used the electron microprobe in their study of liver tissue from a patient dying of DES. They found aluminum present in high concentrations within lipofuscin granules of hepatocytes. This was associated with severe lesions in most hepatic cells, whereas the Kupffer cells remained normal. A similar study using aluminum-intoxicated rats demonstrated the accumulation of aluminum in hepatocyte lysosomes where it forms an insoluble salt with phosphate.

5.4.7 GRANULOMA INDUCTION

Persistent nodules uncommonly follow immunization with diphtheria, tetanus, and pertussis vaccines which contain aluminum hydroxide. Histological studies have suggested a localized response to retained aluminum hydroxide from the vaccines (Savage 1973). Three cases of aluminum hydroxide granulomas have recently been described, and the presence of aluminum was identified by X-ray microanalysis (Slater et al. 1982).

5.4.8 CANCER

A case-control study in Chicoutimi, Quebec, showed there was a high risk of bladder cancer among workers exposed to aluminum emissions, particularly if they smoked (Theriault et al. 1981; Dunkley 1982).

5.4.9 DIALYSIS ENCEPHALOPATHY

Several years after the initiation of dialysis for chronic renal failure, a progressive, fatal encephalopathy was reported in a number of patients from several different dialysis units (Alfrey et al. 1976). The majority of patients in whom the syndrome developed had been on intermittent hemodialyses from 3 to 7 years before the onset of symptoms. All had routinely received aluminum-containing phosphate-binding gels for at least 2 years. The clinical features included a dysarthria-dyspraxia of speech, myoclonus, dementia, focal seizures, and an abnormal encephalogram, showing general slowing and multi-focal loci of theta activity and spikes. Alfrey and co-workers and subsequently several other laboratories reported elevated brain aluminum levels in dialysis encephalopathy, particularly in cerebral gray matter. The mean gray matter aluminum was 2.2 ± 0.7 $mg \cdot kg^{-1}$ (dry weight) in five control subjects, and 25 ± 9.1 (SD) $mg \cdot kg^{-1}$ (dry weight) in patients with encephalopathy, indicating a preferential deposition of aluminum in gray matter. Histological examinations of brains of patients who had encephalopathy did not reveal specific morphological changes; in particular, evidence for a slow viral disease was lacking: injection of brain tissue into primates failed to induce an encephalopathy after 3.5 years. Epidemiological studies have revealed that there is a low incidence of dialysis encephalopathy in treatment centers where the medium for dialysis has low concentrations of aluminum. A lower mean serum aluminum concentration is encountered in centers in which the water employed in dialysis is deionized (Kaehny et al. 1977a). Furthermore, treatment of patients with a trivalent chelating agent, desferrioxamine, has been reported to markedly increase the removal of aluminum and to improve the symptoms of dialysis encephalopathy (Ackrill et al. 1980; Williams et al. 1981).

Most reports in the literature did not find histopathological changes in the brains of individuals with dialysis encephalopathy. However, Brun and Dictor (1981) reported that five of seven brains of patients treated with hemodialysis contained senile plaques and neurofibrillary degeneration. The aluminum content of whole-brain tissue in dialysis encephalopathy is in the range of 15-509 $mg \cdot kg^{-1}$ (dry weight) (Alfrey et al. 1976). In dialysis encephalopathy aluminum appears to remain in the cytoplasm (Crapper et al. 1980). Analysis of seven preparations from five control brains (age range 53-69 years) gave an average intranuclear aluminum content of 716 ± 295 $mg \cdot kg^{-1}$ of DNA compared with 396 ± 134 $mg \cdot kg^{-1}$ for eight preparations from five brains with a clinical history of dialysis encephalopathy. This intracellular distribution differs from an experimental encephalopathy in which aluminum is injected directly into brain or CSF and about 80% of the applied aluminum is found in the nucleus. Five cat brains with aluminum-induced neurofibrillary degeneration had an intranuclear aluminum content of 2582 ± 1763 $mg \cdot kg^{-1}$ of DNA compared with 705 ± 248 $mg \cdot kg^{-1}$ of DNA for control nuclear. Thus the intracellular distribution of aluminum appears to differ in the experimental encephalopathy and in dialysis encephalopathy.

5.4.10 PRIMARY DEGENERATIVE BRAIN DISEASE: SENILE AND PRESENILE DEMENTIA OF THE ALZHEIMER TYPE

Alzheimer's disease is a slowly progressive, fatal polioencephalopathy. The average duration of this untreatable condition is about 10 years. Alzheimer's disease accounts for 60-70% of senile dementia cases and is a major social and medical health problem throughout the world. In North America, Alzheimer's disease is estimated to affect up to 15% of the adult population older than 65 years of age (Wang 1977). Although other body fluids and organs, including serum and spinal fluid, do not appear to have elevated aluminum levels (Crapper et al. 1978; Shore et al. 1980), there is evidence to support the hypothesis that aluminum may contribute to a disorder in neuronal metabolism associated with Alzheimer's disease. In this condition, aluminum is likely to gain access to the central nervous system through an antecedent pathogenic event that either alters brain aluminum metabolism or damages the blood-brain barrier. From this viewpoint, aluminum is considered to be involved in the pathogenesis of the disease, rather than the etiology.

Aluminum, however, does not induce several of the histopathological diseases observed in Alzheimer's disease, such as granulovacuolar degeneration, Hirano bodies, perivascular amyloid, and the amyloid cores within neuritic plaques. Furthermore, neuritic plaques with amyloid cores resembling those found in Alzheimer's disease have been observed in mouse brain infected with the unconventional virus of Scrapie (Bruce and Fraser 1975). There is some circumstantial evidence supporting the possibility that an unconventional virus may also be involved in Alzheimer's disease.

5.4.10.1 Evidence Implicating Aluminum in Alzheimer's Disease

The evidence implicating aluminum as a toxic agent in Alzheimer's disease, perhaps in mechanisms associated with neurofibrillary degeneration, is summarized in Table 5-3.

5.4.10.1.1 Aluminum concentrations in brain tissue. Control human brains in the age range of 50-65 years, completely free of neurofibrillary degeneration (by light-microscopic criteria), have an average aluminum content of 1.9 ± 0.7 mg·kg^{-1} (dry weight) as measured by Crapper et al. (1976) and 2.2 mg·kg^{-1} (dry weight) as measured by Alfrey et al. (1976). McDermott et al. (1977) reported for controls a mean aluminum concentration of 1.53 ± 0.5 mg·kg^{-1} (dry weight) for whole brain and a value for frontal cortex and hippocampus of 1.67 + 0.06. Whereas the mean overall value for 585 samples from 10 Alzheimer-affected brains was 3.8 mg·kg^{-1} Al (dry weight), approximately 30% of the neocortical areas sampled had aluminum concentrations greater than the mean value for controls plus three standard deviations of the mean, or 4 mg·kg^{-1} (dry weight) (Crapper et al. 1976). Elevated aluminum concentrations in Alzheimer's disease were also reported by Trapp et al. (1978).

Table 5-3. Comparison of characteristics of experimental aluminum encephalopathy and Alzheimer's disease.

Experimental aluminum encephalopathy	Alzheimer's disease
1. Toxic concentration to brain: $4\text{-}8\ \mu g \cdot g^{-1}$ Al (dry weight) for cat and rabbit	1. About 30% or more of forebrain gray structures contain $4\ \mu g \cdot g^{-1}$ Al (dry weight) - human fetal neurons in explant respond to aluminum by filament accumulation at $3.3\ g \cdot mL^{-1}$ Al in sediment
2. Progressive encephalopathy - asymptomatic period - progressive memory deficits - focal neurological signs - profound neurological deficits - death 10-28 d	2. Progressive encephalopathy - memory-learning deficits - focal neurological signs - myoclonus - profound neurological deficits - death 2-19 years, average 12 years
3. Neurofibrillary degeneration - 10-nm single filaments - chemical composition closely resembles neurofilaments (68 000; 160 000; 200 000 MW) - immunohistochemically cross-reacts with normal neurofilaments and Alzheimer tangles - "dying back" loss of dendritic complexity	3. Neurofibrillary degeneration - pairs of 10-nm filaments in helical configurations with 80-nm period - chemical composition uncertain - immunohistochemically cross-reacts with normal filaments and aluminum filaments - "dying back" loss of dendritic complexity
4. Accumulates largely upon intranuclear DNA-containing structures; *in vitro* Al^{3+} destabilizes DNA bases and Al(OH)$^{2+}$ binds to phosphate groups	4. Aluminum intranuclear associated with DNA-containing structures - atomic absorption: general increase in region of neurofibrillary degeneration - electron probes: specifically in neurons with neurofibrillary degeneration
5. Reduced nucleolar size in neurons and glia	5. Reduced nucleolar size - neurons with neurofibrillary degeneration - all cells affected in Alzheimer's brain
6. Reduced RNA production in neuroblastoma cells in culture	6. Reduced total RNA
7. Reduced choline acetyl transferase in spinal chord	7. Reduced choline acetyl transferase in forebrain

5.4.10.1.2 Intracellular distribution of aluminum in brain. The increased concentrations of aluminum reported in Alzheimer's disease may be sequestered into tissue compartments different from those in the experimental encephalopathy of animals. However, the intracellular distribution in both conditions is such that aluminum is found mostly in the nucleus. This is consistent with several studies employing histochemical methods and direct quantitative measures of metal content that indicate that aluminum accumulates within the nucleus in plant and animal cells (De Boni et al. 1974; Matsumoto et al. 1976a, b; Crapper and De Boni 1977; Crapper et al. 1980). Direct evidence for intranuclear aluminum in human neurons with neurofibrillary degeneration in both Alzheimer's disease and brains of older individuals considered not to be demented was provided by Perl and Brody (1980).

5.4.10.1.3 Clinical course of Alzheimer's disease and aluminum encephalopathy. Alzheimer's disease usually begins with learning-memory deficits and slowly progresses to involve all aspects of intellectual activity, including judgement, calculation, and language. Motor function is progressively impaired. At variable intervals following the appearance of motor dyspraxia, there is a general increase in muscle tone of an extrapyramidal type and bradykinesia. As the disease progresses, muscle tone increases in intensity, particularly in the flexor groups, resulting in a terminal state of posture in flexion. Myoclonic jerks may be present and seizures occur in perhaps 5-15% of affected individuals. The average duration of the illness is 10 years with a range between 2 and 19 years.

An analogous sequence of events occurs following the intracranial injection of aluminum in susceptible animals such as rabbits and cats. Rats, mice, and certain monkeys, however, are resistant.

After the intracranial injection of a single lethal dose of a soluble salt of aluminum (chloride, lactate, tartrate, or phosphate), both cats and rabbits remain asymptomatic for several days. Performance of delayed response task and a spatial memory task became impaired 8-12 d after the injection in the cat (Crapper and Dalton 1973) and in rabbits (Petit et al. 1980).

Shortly after the appearance of the learning-memory deficit, aluminum-treated animals usually developed myoclonic jerks, ataxia, and a general increase in motor tone. Seizures, unless controlled by anticonvulsant medications, are the usual terminal event 14-28 d after intracranial aluminum injection. Although the time course of the experimental encephalopathy is extremely short, the progression of signs in the animal model mimics those signs found in Alzheimer's disease. This may indicate that either the brain cell populations affected by aluminum resemble those affected in Alzheimer's disease, or that the metabolic insults in these two encephalopathies have similar functional consequences. These observations also indicate that a deteriorating nervous system is not a necessary condition for the expression of aluminum toxicity. Based on the species variation in susceptibility to aluminum, toxicity must also be largely determined by genetic factors.

5.4.10.1.4 **Affected cell populations and neurofibrillary degeneration.** The neuron populations affected by neurofibrillary degeneration in Alzheimer's disease are similar to those induced by aluminum in the brains of cats and rabbits (Ishii 1966; Crapper 1974; Wisniewski *et al*. 1976). Neurons susceptible to neurofibrillary degeneration generally have extensive dendritic trees with large-diameter proximal roots and large-volume somata. The large pyramid-shaped neurons in the neocortex and hippocampal formation and large multipolar cells of thalamus, basal ganglia, and brain stem are affected in both conditions. There are two important exceptions to this generalization: (i) cerebellar Purkinje cells exhibit aluminum-induced neurofibrillary degeneration in animals, but neurofibrillary degeneration has not been observed in these cells for Alzheimer's disease; and (ii) motor neurons of the brain stem and spinal cord exhibit aluminum-induced neurofibrillary degeneration in animals, but these specialized neurons are not affected in humans having Alzheimer's disease. It is noteworthy, however, that in Guam and Kii Peninsula amyotrophic lateral sclerosis, Alzheimer-type neurofibrillary degeneration may occur in motor neurons, and increased aluminum concentrations are found in neurons with neurofibrillary degeneration in the spinal cord and brain system (Yoshimasu *et al*. 1976; Yase 1977; Perl *et al*. 1982).

At the ultrastructural level, the Alzheimer type of neurofibrillary degeneration is composed of paired helical filaments of 10-nm diameter (Wisnieweski *et al*. 1976), whereas the aluminum-induced neurofibrillary tangle is composed of single 10-nm filaments (Terry and Pena 1965; Crapper and Dalton 1973).

5.4.10.1.5 **Reduced choline acetyl transferase.** A biochemical marker for Alzheimer's disease is the reduction in the enzyme that forms acetylcholine, choline acetyl transferase (Davies and Maloney 1976). In the aluminum encephalopathy, spinal cord gray matter and the hypoglossal nucleus were found to have neurofibrillary degeneration, elevated aluminum content, and a decrease in the activities of the enzymes choline acetyl transferase and acetylcholinesterase (Yates *et al*. 1980). Thus, an important marker for the human condition is also found in the experimentally induced aluminum encephalopathy.

5.4.10.1.6 **Dialysis encephalopathy vs. Alzheimer's disease.** Apparently, the normal brain has mechanisms that regulate the turnover of aluminum. When the normal brain is exposed to a large increase in blood-borne aluminum, as occurs in renal failure, the brain aluminum content may increase without signs of neurologic damage until the whole-tissue aluminum exceeds 10-20 times the normal content. Under these circumstances, aluminum accumulates only in the cytoplasm (Crapper *et al*. 1980). By contrast, in

Alzheimer's disease, neither cerebral spinal fluid nor serum aluminum concentrations are elevated. Furthermore, tissues other than the brain do not contain elevated aluminum concentrations, suggesting that blood transport is not defective. Therefore, it is postulated that there exists a primary pathogenic agent in Alzheimer's disease that has altered the blood-brain barrier to aluminum in such a manner that aluminum is not restricted to the cytoplasm where it would normally be rendered harmless. Instead, the element penetrates the DNA-containing structures within the nucleus. Upon gaining access to DNA-containing structures, it is possible that the toxic properties of this element are then expressed. This hypothesis considers aluminum uptake to operate in conjunction with other manifestations of the primary pathogenic event that initiate the neurofibrillary component of the Alzheimer's process.

5.4.11 GUAM PARKINSON-DEMENTIA, AMYOTROPHIC LATERAL SCLEROSIS COMPLEX

On the island of Guam there is an unusually high incidence of amyotrophic lateral sclerosis (ALS) and parkinsonism associated with severe dementia (PD). These neurodegenerative conditions are associated with neurofibrillary degeneration of the Alzheimer type but not senile plaques with amyloid cores. Comparatively high levels of aluminum and manganese and low levels of calcium and magnesium have been found in the drinking water and garden soils of Guam and other high-incidence geographic foci for ALS-PD such as in the Kii peninsula of Japan and Western New Guinea. Yoshimasu et al. (1976), Yase (1977), and Perl et al. (1982) have shown by neutron activation and electron-probe techniques that elevated concentrations of aluminum and calcium occur in the affected tissues compared with age-matched controls. In particular, neurons with neurofibrillary degeneration have remarkably high concentrations of aluminum, in both the nucleus and cytoplasm. It is possible that elevated aluminum in neural tissue is an epiphenomenon accompanying soft-tissue calcification (Yoshimasu et al. 1976). Increasing evidence suggests that a number of affected individuals from Guam have experienced calcium deprivation in the early years of life. This has led to the speculation that aluminum may substitute for calcium, or utilize some of the same transport mechanisms as calcium, to gain access to the brain. These geographically distributed examples of neurodegenerative disease suggest that environment and genetic factors may also determine the expression of aluminum toxicity.

In conclusion, it can no longer be assumed that aluminum is not toxic to humans or that it is not absorbed from the environment. However, further research is needed to establish the exact role this metal may play in human disease.

6.0 ALUMINUM IN THE HUMAN DIET

J.F. Jaworski

National Research Council of Canada
100 Sussex Drive
Ottawa, Ontario K1A 0R6

6.1 NATURAL LEVELS

Aluminum is naturally present at low levels in most foods (Sorenson et al. 1974; see Tables 6-1 and 6-2). Unrefined plant products appear to contain the highest levels of aluminum, and infusions derived from plant material may also contain significant quantities of aluminum (e.g., a single cup of tea may contain 0.5 mg Al; Stagg and Millin 1975).

The aluminum concentration in raw surface water lies in the range <0.05-10 $mg \cdot L^{-1}$, whereas that in typical drinking water is in the range <0.001-1.6 $mg \cdot L^{-1}$. The aluminum levels in water are determined by the biogeochemical factors described in Chapter 2.

6.2 ALUMINUM ADDITIVES

Lione (1983) listed the six aluminum salts approved as food additives, as well as the amounts used and expected levels in the food (see Table 6-3). Processed cheese slices can each contain 50 mg Al (added as sodium aluminum phosphate at a level of 3% by weight to act as an emulsifier). An average serving of cake prepared with aluminum-containing baking powder may contain 5-15 mg Al. A medium-sized pickled cucumber soaked in a 0.1% aluminum ammonium sulfate solution may contain 5-10 mg Al. Aluminum silicates are used at levels of up to 2% by weight as anticaking agents in powdered soups, nondairy creamers, and other dry, powdered products. Chewing gum may contain 3.0-4.5 mg Al per 5-g stick, and the amount extracted by chewing ranges between 0.011 and 0.45 mg Al per stick (Lione and Smith 1982; Lione 1983).

6.3 ESTIMATED DAILY INTAKE

Sorenson et al. (1974) estimated from total-diet studies that the average adult consumes 5-10 $mg \cdot d^{-1}$ Al. This implies that high-aluminum foods do not constitute an important part of the diet for most people; however, as seen in Section 6.2, consumption of certain foods can easily double or triple the daily aluminum intake.

6.4 ALUMINUM IN NONPRESCRIPTION DRUGS

A number of nonprescription drugs, such as antacids, buffered aspirin, antidiarrheals, etc., may contain considerable amounts of aluminum

Table 6-1. Aluminum concentrations in different classes of food not containing aluminum as a food additive (from Sorenson et al. 1974).

Foods	Aluminum concentration[α] (mg·kg^{-1} (wet weight))
Cereal and products	0.02-5.4
Vegetables	<0.10-4.8[β]
Fruits	<0.10-2.68
Herbs and spices	20-700
Nuts	<2.0
Oils	0.08-0.40
Sugars	0.22-2.27
Dairy products	0.15-20[γ]
Meats and meat-vegetable combinations	<1.0
Poultry	0.20-1.40
Fish and shellfish	0.70-1.40[δ]
Miscellaneous[ε]	<0.4-50

[α] Data from U.S.S.R. are much higher and have been mostly excluded.

[β] Sporadic elevation was found in spinach, asparagus (up to 20 mg·kg^{-1}), and in jelly, juice, and canned plums (up to 14 mg·kg^{-1}).

[γ] Cow's milk: 0.15-0.97 mg·kg^{-1}; butter milk and cheese: 2-20 mg·kg^{-1}.

[δ] Some canned fish up to 8.2 mg·kg^{-1}; see also Table 6-2.

[ε] Includes coffee, tea, and cocoa.

Table 6-2. Aluminum concentrations in fish and shellfish (from Sidwell *et al*. 1978).

Species	Aluminum concentration (mg·kg^{-1} (wet weight))
Catfish	0.9
Cod	2.5
Codfish	4.1
Crab	35.9
Crayfish	45.9
Cusk eel and brotula	1.8
Cutlassfish and hairtail	1.8
Eel, conger	2.8
Flounder	1.0-11.0
Gar	2.6
Gobies and grenadier	1.9
Grunt	2.6
Haddock	0.3
Jack and pomano	5.3
Mackerel and tuna	1.2-178.2
Minnow and carp	1.3-46.1
Mussels	2.9
Oysters	13.4
Sable fish	3.1
Sauries	1.1
Sea cucumbers	43.8
Sharks	11.5
Squid	17.5
Trout and salmon	2.1

Table 6-3. Aluminum-containing food additives permitted in the U.S.A. and Canada (from Lione 1983).

Compound	Aluminum concentration (% by weight)	Total food use in 1970, U.S.A. (kg)[α]	Common uses (maximum concentrations)	Aluminum content in product
Sodium aluminum phosphates	6.5[β]	18 000 000	In cake mixes, frozen dough, self-raising flour In processed cheese (3.3-5%)	5-15 mg/serving 50 mg/slice
Sodium aluminum sulfate	5.9	3 600 000	In household baking powders (21-26%)	70 mg/tsp.[γ] 5 mg/serving
Aluminum sulfate	1.3	510 000	As food starch modifier	-
Aluminum ammonium sulfate	6.0	230 000	In pickling salts (0.1%)	-
Aluminum potassium sulfate	5.7	3 800	In pickling salts (0.1%)	-
Sodium aluminum silicate	16	NA[δ]	As anticaking agent (2%)	-
Aluminum calcium silicate	17	NA	As anticaking agent (2%)	-
Sodium calcium aluminosilicate (hydrated)	12	NA	As anticaking agent (2%)	-

[α] Mean value.

[β] Serving of cake made with 1 tsp. baking powder.

[δ] NA = not available.

[γ] tsp. = teaspoonful.

(see Table 6-4). Continuous or frequent use of these products can increase the daily aluminum intake by a factor of 10-100.

6.5 ALUMINUM UPTAKE

Very little aluminum is absorbed from the gut in normal humans. Balance studies indicate that even at 125 $mg \cdot d^{-1}$ Al given as aluminum lactate (1.8 $mg \cdot kg^{-1} \cdot d^{-1}$ Al), fecal and urinary aluminum excretions were approximately equal to the intake (Greger and Baier 1983). Studies with rats and dogs indicate that tissue aluminum levels increased significantly when dietary aluminum levels (given as $AlCl_3$ or $Al(OH)_3$) reached 40-60 $mg \cdot kg^{-1} \cdot d^{-1}$ Al (Arieff et al. 1979; Bowdler et al. 1979). This is the equivalent of 3-4 $g \cdot d^{-1}$ Al intake by the average human adult.

6.6 ALUMINUM COOKWARE AND FOIL WRAP

Cooking salty, acidic, or alkaline foods on aluminum cookware or storing such foods in direct contact with aluminum foil can increase aluminum levels in the table-ready product (Sorenson et al. 1974; Lione 1983). The amount of aluminum added depends on many factors, such as the pH, temperature, and salt content of the food, as well as the purity of the aluminum in the "curing" of the cooking surface. A maximum contribution from this source was estimated at 20% of the total daily aluminum intake (Lione 1983). The introduction of Teflon-coated aluminum cookware has significantly decreased aluminum contributions from this source.

Table 6-4. Nonprescription drugs that contain aluminum (from Lione 1983).

Drug class	Aluminum salts used	Aluminum per dose (mg)
Antacids	Aluminum hydroxide	35-208
	Dihydroxyaluminum acetate	45-72
	Aluminum carbonate	NA[α]
	Aluminum oxide	41
	Bismuth aluminate	55
	Magaldrate	51-61
	Dihydroxyaluminum aminoacetate	100
	Dihydroxyaluminum sodium carbonate	63
Internal analgesics - buffered aspirins	Aluminum hydroxide	9-52
	Aluminum glycinate	10-15
Antidiarrheals	Kaolin	120-1450
	Aluminum magnesium silicate	36
	Attapulgite	500-600
Douches	Ammonium aluminum sulfate (5-16%)	NA
	Potassium aluminum sulfate	NA
Hemorrhoidal medications	Aluminum hydroxide	NA

[α] NA = not available.

7.0 THE DETERMINATION OF ALUMINUM IN ENVIRONMENTAL SAMPLES

J.F. Jaworski

National Research Council of Canada
100 Sussex Drive
Ottawa, Ontario K1A 0R6

7.1 INTRODUCTION

This chapter deals primarily with methodology for determination of the element aluminum in various matrices. Chemical extraction procedures must be coupled to these methods in order to determine what fraction of the total aluminum in the sample is biologically available. Aluminum speciation is discussed in Chapters 1 and 2.

7.2 POSSIBLE ERRORS IN ALUMINUM ANALYSIS

7.2.1 CONTAMINATION

Errors may occur at any of the steps involved in the analytical process: sampling, storage, treatment, measurement. Contamination is the most serious problem encountered because aluminum is ubiquitous and often found in high concentrations (Versieck and Cornelis 1980). Table 7-1 lists some sources of aluminum contamination that may be found in the laboratory.

7.2.1.1 Contamination from Dust

Airborne particles, both natural and man-made, often contain several percent concentrations of aluminum (Zief and Mitchell 1976). These may lead to severe contamination problems unless dust control measures are implemented as in a clean room facility. Air-conditioning systems and air filters often contain aluminum parts that may corrode and eventually contribute to the aluminum dust load. The use of alumina-based abrasives, desiccants, or column packing in adjoining laboratories may contribute significantly to levels of aluminum found in fine dust particles, and may result in a highly variable background or blank value (Zief and Mitchell 1976).

7.2.1.2 Contamination of Laboratory Reagents

Commercially available reagents and water purification media contain trace levels of aluminum (see Table 7-2). The materials from which reagent containers are made also contribute to analytical background levels. Most types of glass contain several percent concentrations of aluminum (Table 7-3) which may be leached out by acids. Zeif and Mitchell (1976)

Table 7-1. Sources of aluminum contamination.

Source	Reference
Air	
Soil particles, dust	
High-temperature emissions	
Corroded air-conditioning cooling fins	
Powdered alumina (desiccant, GC column packing or abrasive)	
Reagents	
Some glass and plastic containers	Hydes and Liss 1976
Formaldehyde stored in Al container	
Acid, distilled water	Hydes and Liss 1976
Buffers	Kramer *et al*. 1981
Colorimetric agents	Kramer *et al*. 1981
Commercially available nucleotides	Tornheim *et al*. 1980
Reagent-grade alkali and alkaline metal chloride	Bloom *et al*. 1978
Apparatus	
Porcelain mortar and pestle	
Rubber tubing, stoppers, or bulbs	
Filtering media	
Ion-exchange resin	
Al foil, tubing, gas cylinders	
High-temperature liners of muffle furnaces	

Table 7-2. Aluminum in some commercially available acids, distilled water, and ion-exchange resins (from Blotcky *et al*. 1976).

Sample	Al concentration ($mg \cdot L^{-1}$)
Concentrated HNO_3 (ultrapurity)	0.02
Concentrated HNO_3 (analytical grade)	0.1-0.3
Concentrated HF (analytical grade)	0.25-0.69
Distilled water	0.01-0.03
Ion-exchange resins	0.25-4.7[α]

[α] Units are $mg \cdot kg^{-1}$.

Table 7-3. Aluminum concentrations in glass (from Zief and Mitchell 1976).

Type of glass	Aluminum concentration (%)
Soda lime	1-2
Borosilicate	2-6
Chemically strengthened	20
High silica	0.5
Vitreous silica	0

(1976) reported that concentrated HCl leached 23 $\mu g \cdot L^{-1}$ Al from borosilicate glass in 2 d, whereas 10 $\mu g \cdot L^{-1}$ Al was leached from the same glass which had been pretreated with acid. It appears that glass is an unsuitable material to be used in apparatus for the analysis of low levels of aluminum because it either contributes a significant background to acid solution or, when pretreated with acid, causes aluminum loss by adsorption from solution (e.g., see Ritchie *et al*. 1980).

Compared with glass, plastics have much lower concentrations of aluminum (see Table 7-4), either from residues of polymerization catalysts or from the abraded surface of metal molds containing aluminum. For example, microscopic particles found less than 7 µm below the surface of Teflon (FEP) bottles contain aluminum abraded from the metal mold (Zief and Mitchell 1976). Several nanograms of aluminum per square centimetre of plastic surface may be leached from the surface of new plastic bottles (see Table 7-5). However, once aluminum has been leached from the plastic surface (using acid (1+1) HCl followed by (1+1) HNO_3 and ultrapure water as recommended by Moody and Lindstrom 1977), there is less tendency for the plastic to adsorb aluminum from solution, especially if the pH is kept below 2.5 (Subramanian *et al*. 1978). Colloidal aluminum species, which form at more basic pH values, adsorb into the walls of LPE (linear polyethylene) containers so that almost half of the 100 $\mu g \cdot L^{-1}$ Al in river water (pH 6.7) was lost from solution by adsorption (Benes and Steinnes 1975). From these considerations it appears that CPE (conventional polyethylene) is the best material from a cost/performance viewpoint when storing aqueous reagents for aluminum analysis.

7.2.1.3 Contamination from Laboratory Apparatus Containing Aluminum

Much of the apparatus commonly used in the laboratory contains high concentrations of aluminum. Some materials, such as glass, porcelain (mortars and pestles), and alumina (muffle furnace liners), contain aluminum in a relatively insoluble form; however, if particles of these become mixed with the sample, a number of methods such as neutron activation, X-ray fluorescence, arc emission, and spark-source mass spectrometry will measure the contaminant aluminum along with that present in the sample. For example, Ihnat (1976) reported an analytical blank of 4 $\mu g \cdot L^{-1}$ Al for Teflon sample digestion flasks, but 10 times that level when samples were digested in Pyrex vessels. Rubber (gloves, stoppers, bulbs) contains leachable aluminum added as either accelerator or catalyst. In addition, many new rubber products come coated with talc which contains aluminum. Aluminum metal is used in gas cylinders, tubing, and Eppendorf pipettes, as well as metallic aluminum foil to keep dust off samples and to line organic reagent bottle caps. Material abraded from these objects or aluminum leached from contact with these surfaces is another source of contamination.

Materials used for filtering air or aqueous solution often contain aluminum which can be transferred physically or chemically to the sample (see Table 7-6). Kramer *et al*. (1981) reported that when 250 mL of an

Table 7-4. Aluminum concentrations in plastic (from Moody and Lindstrom 1977).

Type of plastic	Aluminum concentration ($mg \cdot kg^{-1}$)
Polypropylene (PP)	55.0
Linear polyethylene (LPE)	30.0
Teflon sealing tape (TPT)	29.0
Polymethylpentane (PMP)	6.2
Polycarbonate (PC)	3.0
Conventional polyethylene (CPE)	0.50
Polystyrene (PS)	0.50
Teflon (TFE)	0.23
Teflon (FEP)	0.20

Table 7-5. Leaching of aluminum from the surface of plastic bottles (from Moody and Lindstrom 1977).

Type of plastic bottle	Aluminum leached by acid after 1 week ($ng \cdot cm^{-2}$)	
	(1+1) HCl	(1+1) HNO_3
Teflon (FEP)	4	6
Linear polyethylene (LPE)	4	1
Conventional polyethylene (CPE)	10	1
Polycarbonate (PC)	3	5

Table 7-6. Aluminum concentrations in filtering media.

Type of filter	Aluminum concentration	Reference
Nitex (Teflon)	$8\ \mathrm{mg \cdot kg^{-1}}$	Zief and Mitchell 1976
Whatman 541 (cellulose)	$1\ \mathrm{mg \cdot kg^{-1}}$	Zief and Mitchell 1976
Nuclepore (0.1 μm)	$0.7\text{-}6\ \mathrm{ng \cdot cm^{-2}}$	Rosenberger *et al*. 1979
Glass fiber	$2\text{-}30\ \mathrm{\mu g \cdot cm^{-2}}$	Rosenberger *et al*. 1979
Durethene[α]	$0.8\ \mathrm{mg \cdot kg^{-1}}$	Rosenberger *et al*. 1979
Handiwrap[α]	$0.05\ \mathrm{mg \cdot kg^{-1}}$	Rosenberger *et al*. 1979

[α] Plastic film used to collect cascade impactor samples.

aqueous sample was filtered through a 0.45-μm pore membrane filter, the resultant contamination was approximately 1 $\mu g \cdot L^{-1}$ Al. Filters prewashed with acid contributed less than half that amount of aluminum.

7.3 SAMPLING AND SAMPLE STORAGE

7.3.1 AQUEOUS SAMPLES

In Section 7.2.1.2, acid-cleaned polyethylene or Teflon FEP containers were identified as those least likely to contaminate aqueous solutions with aluminum or remove aluminum by adsorption. At pH 2.5, hydrated aluminum species slowly polymerize so that it may take 10 d or more for colloidal particles as large as 0.1 μm to form (Hem 1968a). Once formed, these colloids tend to absorb onto the container walls (Benes and Steinnes 1975). Thus aluminum solutions are most stable at pH values below 1.5 or above 12.0, where aluminum colloids are not likely to form (Zief and Mitchell 1976). However, addition of acid or base will preclude determination of the aluminum species originally present. Nitric acid is preferred to HCl in sample stabilization; this minimizes problems from the formation of volatile $AlCl_3$ (sublimes 177.8°C).

7.3.2 BIOLOGICAL SAMPLES

Little aluminum contamination is expected from the use of clean stainless steel sampling utensils or from the use of acid-washed polyethylene (CPE) storage containers. Tissues should be stored frozen or freeze-dried (avoid aluminum-containing desiccants) rather than fixed with formalin or ethanol which may result in contamination or loss (formaldehyde is often supplied in aluminum bottles).

7.3.3 GEOLOGICAL SAMPLES

Because most rocks, soils, and sediments contain several percent concentrations of aluminum, contamination poses much less of a problem, and thus cleaned glass containers may be used for sample storage.

7.4 SAMPLE TREATMENT PRIOR TO ANALYSIS

The halides $AlCl_3$ (sublimes 177.8°C), $AlBr_3$ (boils 263°C), and AlI_3 (boils 360°C) are the most commonly encountered volatile compounds of aluminum. If possible, additions of these halogens to the sample should be avoided to prevent losses during ashing or when aqueous samples are heated to dryness (as in the case of graphite furnace atomic absorption).

Refractory geological samples pose problems, especially if the sample size is small (as in particulate matter trapped on filter media).

Preseparation of aluminum from other elements is usually difficult; it is better to choose an instrumental method with the required atomic selectivity rather than to chemically isolate the aluminum in the sample. Young (1980) outlined some of the classical procedures whereby aluminum can be isolated from certain special types of sample.

Boric acid should not be included in fluxing mixtures because it usually contains an aluminum impurity, whereas HF should be used sparingly because it forms a stable complex with aluminum which may cause difficulty during the determination step, e.g., in flameless atomic absorption (Eggimann and Betzer 1976).

7.5 MEASUREMENT TECHNIQUES

7.5.1 ATOMIC ABSORPTION (AA)

7.5.1.1 Flame Atomization

A nitrous oxide - acetylene flame atomizes aluminum more efficiently than do other types of flames (David 1980). Using an acetylene-rich flame, a detection limit of 0.2 $mg \cdot L^{-1}$ may be achieved for the analytical wavelength of 309.3 nm (Price 1972). Calcium, silicon, chloride, and perchlorate depress the aluminum absorption signal, whereas titanium, iron, fluoroborate, and acetic acid enhance it (Price 1972). Ionization of aluminum can be controlled using 3 $g \cdot L^{-1}$ K^+ (David 1980). Signal depression by calcium and other inorganic components in plant tissue can be overcome by adding sulfuric acid (2% by volume, final concentration) and 1 $g \cdot L^{-1}$ Mo (David 1980). The use of diphenylthiocarbazone or 8-hydroxyquinoline to chelate the aluminum with subsequent extraction into benzene can improve the detection limit to 9 $\mu g \cdot L^{-1}$ Al (Hsu and Pipes 1972). Bower and Ingle (1979) studied the major factors that limit the precision of flame AA analysis for aluminum. These include flame flicker, amplifier noise, and photomultiplier shot noise. Brodie and Liddell (1980) discussed the use of Zeeman-effect background correction to improve accuracy and detection limits in flame AA.

7.5.1.2 Graphite Furnace Atomization

The alignment rod supplied with a number of graphite furnaces is made of aluminum; this should be replaced by one made from glass or another metal not containing aluminum (Gorsky and Dietz 1978). Another source of contamination is the disposable plastic tip on the Oxford microlitre pipette. This contaminant can be minimized by prewashing the tips with an EDTA solution (Gorsky and Dietz 1978). Leung and Henderson (1982) reported that the matrix effect could be eliminated in graphite furnace determinations of aluminum by using a stabilized temperature platform.

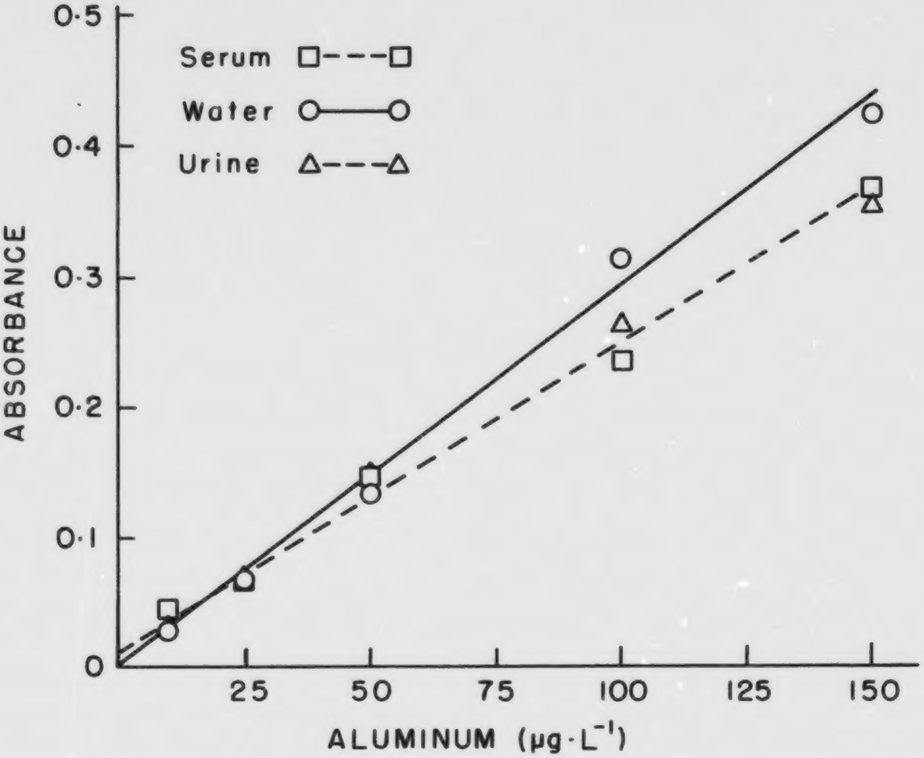
Sturgeon (1977) reviewed the factors affecting atomization and measurement in graphite furnace AA. Any reaction interfering with the formation of aluminum atoms will result in a matrix effect which is often observed with furnace atomizers. Figure 7-1 shows that the response for aluminum in distilled water is different from that for aluminum in blood serum or urine. This matrix effect is probably in part because of chloride ion in the serum and urine, which causes volatile $AlCl_3$ to be lost during the ashing step. The effect can be overcome by swamping out the chloride with known amounts of SO_4^{2-} (Gorsky and Dietz 1978) or with $(NH_4)_2$ EDTA (EDTA complexes the aluminum whereas the NH_4Cl is easily volatilized; Matsusaki et al. 1979). Perchloric acid ($HClO_4$) residue, from the wet ashing of organic material, strongly suppresses the absorption signal for aluminum by forming an unknown product with the graphite surface which forms a nonatomizing adduct with aluminum in the gas phase. $(NH_4)_2SO_4$, added to samples and standards, reduces the signal suppression (Koirtyohann et al. 1981). Persson et al. (1977) observed that oxygen, hydrogen, or nitrogen gas in the graphite furnace suppresses the absorption signal of aluminum by forming molecular species which diffuse out of the furnace before decomposing to yield Al atoms. This effect can be minimized by using argon gas to purge air out of the furnace. Sulfur in the sample can also depress the atomic absorption signal for aluminum by forming Al-S species. This effect is minimized at high ashing temperatures (about 1250°C). Table 7-7 gives some examples of analysis of biological materials using the graphite furnace atomizer. Note the lower detection limit ($<10^{-15}$ g) reported for the determination of aluminum in distilled water. Background absorption and matrix effects make the detection limit with environmental or biological samples much higher ($<10^{-11}$ g), although the capacitive discharge system described by Chakrabarti et al. (1980) may lower this significantly. Zeeman-effect background correction has shown great promise in overcoming the large background signal encountered in the analysis of aluminum in organic matrices (Koizumi et al. 1977; Fernandez et al. 1980). Reactions that interfere with aluminum atom function may be used to advantage, as in the method of Tsunoda et al. (1977). In this study a detection limit of 3×10^{-11} g Al was reported from measurement of absorbance of the AlF molecule at 227.5 nm.

7.5.2 ATOMIC EMISSION SPECTROSCOPY (AES)

Emission spectroscopy not only permits sensitive determination of aluminum but, in principle, also allows for the simultaneous determination of a number of other elements. In contrast, atomic absorption usually permits the determination of elements only one at a time.

7.5.2.1 Flame Emission

Using a nitrous oxide - acetylene flame, it is possible to detect as little as 0.05 $mg \cdot L^{-1}$ Al in blood plasma by emission spectroscopy (at 396.2 nm); however, problems with flame background make the use of background correction mandatory, and this limits sensitivity (Ihnat 1976).



Matrix	Slope x 10^3	y-intercept x 10^3	r
Serum	2.36	11.68	0.9953
Water	2.92	-1.31	0.9971
Urine	2.38	11.72	0.9948

Figure 7-1. Standard curves showing the effects of different matrices on the aluminum signal (from Gorsky and Dietz 1978).

Table 7-7. Examples of aluminum analyses performed using graphite furnace atomizers.

Sample type	Comment on methodology	Detection limit	Reference
Dried soft tissue	Dry ash in platinum crucible at 650°C; dissolve ash in 5% HNO_3	10^{-11} g (0.3 $mg \cdot kg^{-1}$ in 30 mg)	Krishnan _et_ _al_. 1976
Blood plasma	Direct analysis	3 x 10^{-11} g (1.2 $\mu g \cdot L^{-1}$)	Gorsky and Dietz 1978
Whole blood	Direct analysis	0.05 $mg \cdot kg^{-1}$	Langmyhr and Tsalev 1977
Blood serum	Dilute using EDTA-NH_4OH-H_2SO_4-Triton X	0.002 $mg \cdot kg^{-1}$	Alderman and Gitelman 1980
Freeze-dried tissue	Wet ash in platinum crucible	4 x 10^{-1} g (0.1 $mg \cdot kg^{-1}$)	Julshamn _et_ _al_. 1978
Blood serum	Wet ash in platinum crucible	4 x 10^{-11} g (0.01 $mg \cdot kg^{-1}$)	Julshamn _et_ _al_. 1978
Aqueous solution (synthetic sample)	Graphite furnace heated by capacitive discharge	2 x 10^{-15} g	Chakrabarti _et_ _al_. 1980
Blood serum	Fractionated by gel filtration interfaced to graphite furnace by autosampler	0.4 $\mu g \cdot L^{-1}$	Toda _et_ _al_. 1980

7.5.2.2 Furnace Emission

Detection limits of approximately 0.04 $\mu g \cdot L^{-1}$ Al were reported using the graphite furnace as excitation source (Epstein et al. 1978; Ottaway et al. 1980). However, this low detection limit was reported for a dilute aqueous solution and it would be expected to increase significantly for a more complex matrix such as an acid digest of blood plasma. As in the case of graphite furnace atomic absorption, aluminum can be lost prior to the atomization step if volatile $AlCl_3$ is formed (Epstein et al. 1978). Similarly, other significant matrix effects may be expected. Careful calibration with standard reference materials, therefore, is mandatory. Because this method can also be used to analyze some solid samples directly (e.g., freeze-dried tissue, blood), the possibility of loss or contamination during pretreatment can be minimized.

7.5.2.3 Inductively Coupled Plasma (ICP) Emission

The plasma emission source (Fassel and Knisseley 1974) offers a somewhat poorer (but adequate) detection limit for aluminum than does the graphite furnace (range 0.5-5 $\mu g \cdot L^{-1}$ Al depending on matrix), but because it achieves a much higher excitation temperature than does the graphite furnace it has the advantage of being relatively free of interferences and matrix effects (see Table 7-8 and Figures 7-2 and 7-3 for examples of these effects). Thus, more reliable and precise results may be obtained with complex samples such as coal and fly ash (Nadkarni 1980), used engine oil (Merryfield and Lloyd 1979), blood and wine (Allain and Mauras 1979; Lichte et al. 1980), and geological samples (Burman and Bostrom 1979). Solid samples must first be dissolved and nebulized (made into a fine spray) before introduction into the plasma.

7.5.2.4 Direct Current (DC) Plasma Arc Emission

The DC plasma arc source is similar to the ICP source with the exception that the plasma is maintained directly by a unidirectional flow of electric current rather than indirectly by electromagnetic induction. As in the case of ICP, easily ionized elements enhance the signal derived from a given concentration of aluminum (Table 7-9). The method has been applied to the determination of aluminum in water (Johnson et al. 1979) and in dissolved geological samples (Bankston et al. 1979).

7.5.2.5 Gas Chromatography/Emission Spectroscopy

Van Loon (1979) reviewed aspects of metals analysis and speciation using coupled chromatographic and atomic spectroscopic techniques. One advantage of these methods is that chromatographic preseparation decreases the background signal to such an extent that limits of detection are greatly

Table 7-8. Some interferences and matrix effects in plasma emission determination of aluminum.

Interference or matrix	Effect on signal intensity	Aluminum spectral line (nm)	Reference
Ca	Increases background from stray light	394.4	Lichte *et al.* 1980
Ca	Increases background equal to 2.6 $ng \cdot L^{-1}$ Al per $\mu g \cdot L^{-1}$ Ca	396.2$^{\alpha}$	McQuaker *et al.* 1979
Mo	Increases background equal to 28 $ng \cdot L^{-1}$ Al per $\mu g \cdot L^{-1}$ Mo	396.2	McQuaker *et al.* 1979
Alkali and alkaline metal ions	Increases signal by 20-30% at 10 $mg \cdot L^{-1}$	396.2	Allain and Mauras 1979
B	Increases signal at 1 $mg \cdot L^{-1}$ B	396.2 394.4	Allain and Mauras 1979
Cu	Depresses signal at 250 $mg \cdot L^{-1}$ Cu	396.2	Allain and Mauras 1979
K	Depresses signal at 200 $mg \cdot L^{-1}$ K	396.2	Merryfield and Lloyd 1979
Distilled water	Detection limit is 0.4 $\mu g \cdot L^{-1}$ Al	396.2	Allain and Mauras 1979
Urine	Detection limit is 1.0 $\mu g \cdot L^{-1}$ Al	396.2	Allain and Mauras 1979
Blood	Detection limit is 4 $\mu g \cdot L^{-1}$ Al	396.2	Allain and Mauras 1979

[α] Stray light from the Ca line at 393.3 nm contributes in a major way to background at this Al line.

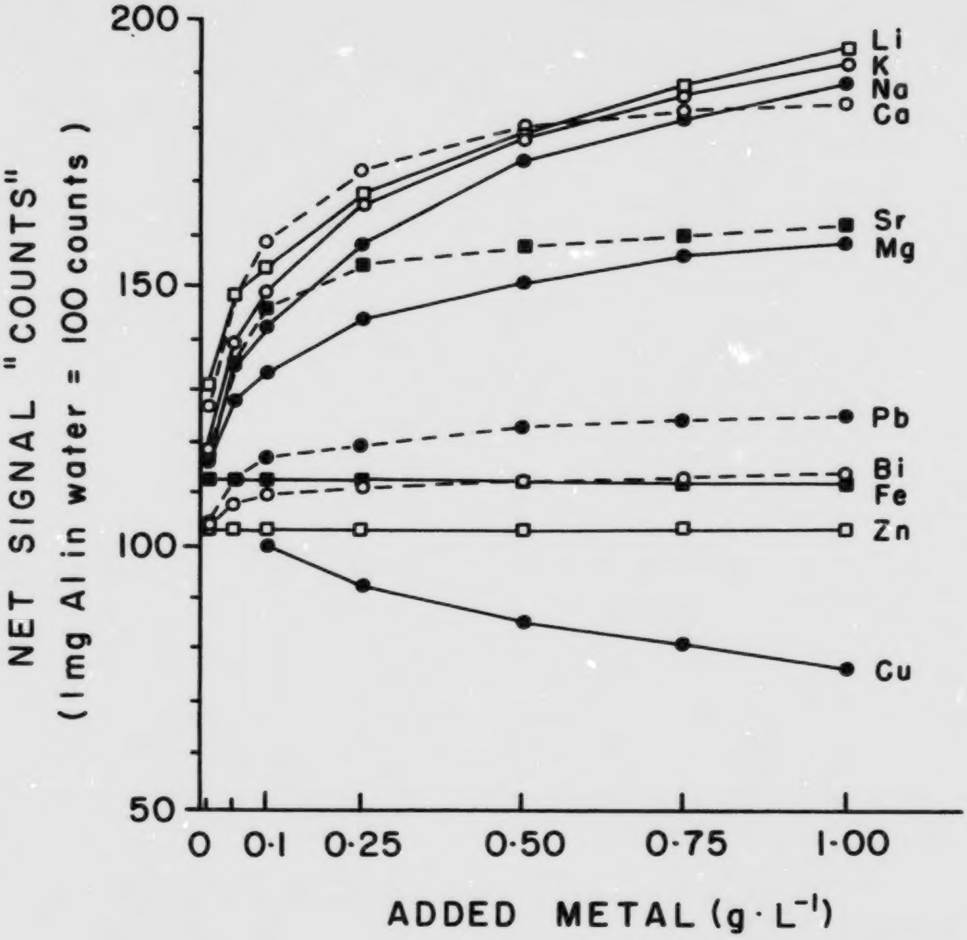


Figure 7-2. Influence of different metals on the ICP signal intensity from a 1 mg·L^{-1} Al solution (from Allain and Mauras 1979).

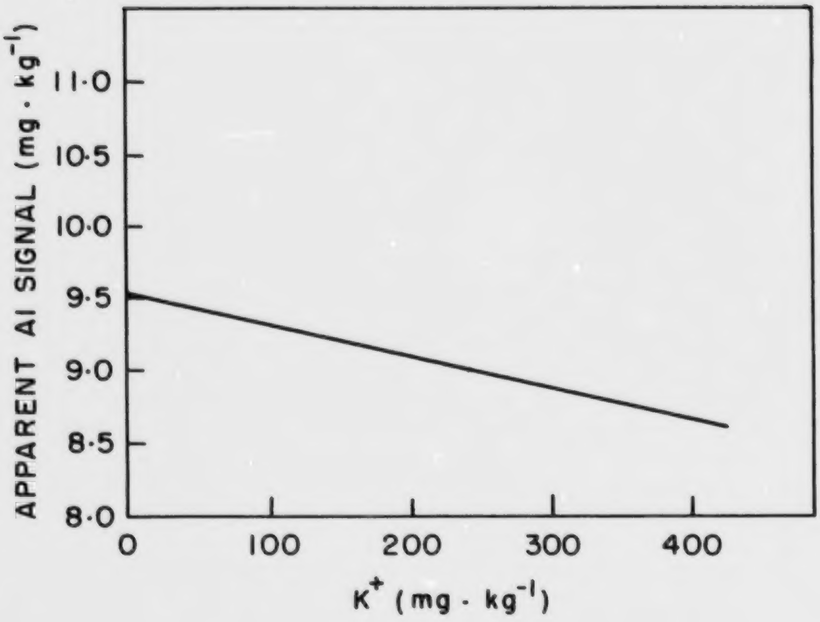


Figure 7-3. Effect of potassium (K^+) on the emission intensity of aluminum atoms at 396.2 nm (from Merryfield and Lloyd 1979).

Table 7-9. Aluminum signal enhancement by easily ionized elements in direct current plasmas (from Nygaard and Gilbert 1981).

Element[α]	Relative strength of the aluminum signal[β]
K	1.70
Sr	1.68
Mg	1.55
Cd	1.32
Hg	1.31

[α] Elements all present as chlorides at a concentration of 0.1 M.

[β] At wavelength 394.4 nm.

improved. Dagnall et al. (1973) used a gas chromatograph coupled to a microwave plasma emission spectrometer to detect as little as 2.0×10^{-11} g Al present as the acetylacetone chelate.

7.5.2.6 Laser Probe/Emission Spectroscopy

The pulse sampling obtained by using a laser to vaporize about 1 µg of a sample surface permits detection of very low levels of aluminum and other elements because of the almost instantaneous production of large numbers of atoms and ions. The addition of a microwave-induced plasma excitation source improves the detection limits, as in the method of Ishizuka and Uwamino (1980) where a laser probe/microwave plasma emission source permitted the analysis of $(10\text{-}13) \times 10^{-12}$ g (10-13 $\text{mg}\cdot\text{kg}^{-1}$ in a 1-µg sampling) aluminum in brass.

7.5.3 SPECTROPHOTOMETRY

A number of organic molecules form intensely colored complexes with aqueous aluminum ions. The absorbance of these molecular complexes may be used to detect rather low concentrations of aluminum (0.5-5 $\mu\text{g.L}^{-1}$ Al) in aqueous solution or in organic-phase extracts of these solutions. Table 7-10 gives some examples of spectrophotometric methods for determination of aluminum. The methods, as indicated in Table 7-10, are specific for aluminum only insofar as interfering cations and anions are chemically separated or masked before the color-producing agent is added. Thus, in experienced hands, they may give results comparable in sensitivity to those from atomic absorption or atomic emission spectrometry.

7.5.4 FLUORESCENCE METHODS

7.5.4.1 Fluorometry

Aluminum forms fluorescent aqueous complexes with certain organic molecules. The intensity of the fluorescence is a measure of the aluminum concentration. Because the technique has an inherently better signal-to-noise ratio than does spectrophotometry, it has lower detection limits (0.05-5 $\mu\text{g.L}^{-1}$ Al; see Table 7-11). However, interference is the same as in the spectrophotometric determination of aluminum (Table 7-11).

7.5.4.2 Atomic Fluorescence Spectrometry

If aluminum atoms in the gas phase are irradiated with light of a certain frequency they fluoresce. One problem with atomic fluorescence has been a poor detection limit because the analyte atoms are very widely dispersed. Detection limits can be improved by using a laser to increase the photon density of the light which excites the fluorescence. Thus, Weeks

Table 7-10. Spectrophotometric determination of aluminum.

Complexing agent	Matrix	Detection limit$^{\alpha}$	Interferences	Reference
8-hydroxyquinoline$^{\alpha}$	Natural waters	0.2 $\mu g \cdot L^{-1}$	V, Fe, Ni, Cu, Ga, Mo, U, F	May *et al.* 1979a
"	Soil extracts	50 $\mu g \cdot L^{-1}$	F, Cu, PO_4^{3-}, Zn, Mn	Bloom *et al.* 1978
Pyrocatechol violet$^{\gamma}$	Natural waters	5 $\mu g \cdot L^{-1}$	F	Henriksen and Bergmann-Paulsen 1975
Chrome azurol S/ N-phenylbenzoyl-hyroxamic acid$^{\delta}$	Biological tissues; natural waters	2 $\mu g \cdot L^{-1}$	F	Que Hee and Finelli 1980
Pyrocatechol violet/zephiramine$^{\delta}$	Natural waters	3 $\mu g \cdot L^{-1}$ (10 mg)	Fe, F	Korenaga *et al.* 1980
Chromazurol S	Ceramics	1 μg	Zr, rare earths	Kruidhof 1978
Erichrome cyanine R$^{\gamma}$	Plant tissue; soil extracts	0.5 $mg \cdot L^{-1}$	Fe, PO_4^{3-}	Reis *et al.* 1979
Alizarin red S$^{\delta}$	Plant tissue; soil extracts	0.5 $mg \cdot {}^{-1}$	Fe, PO_4^{3-}	Lancaster and Balasubramanian 1974

[α] Numbers not in parentheses are concentration detection limits; those in parentheses are absolute detection limits.

[β] The complex formed was extracted into an organic solvent prior to measurement.

[γ] Automated method processing 30 samples per hour.

[δ] A liquid-ligand interchange complex is formed.

Table 7-11. Fluorimetric determination of aluminum.

Complexing agent	Matrix	Detection limit[α] ($\mu g \cdot L^{-1}$ Al)	Interferences	Reference
3-Hydroxypyridine-2-aldehyde-2-pyridylhydrazone	Natural water	2 (50 ng)	0.5 $mg \cdot L^{-1}$ of Co, Ni, Cu, Pb, Zn, Mn, F 1-100 $mg \cdot L^{-1}$ of Hg, Cr, In, Cd, Zr, Ga, Th, Be, Ag, Y	Cano-Pavon *et al*. 1980
Morin	-	(0.5 ng)	-	Udenfriend 1962
Lumogallion (+ surfactant)[β]	-	0.5		Ishibashi and Kina 1972
8-Hydroxyquinoline	Soil extracts	0.3	F, PO_4^{3-}, Fe	Bloom *et al*. 1978
Lumogallion	Plants, soils, irrigation	0.6 (0.03 μg)	Mo, SiO_3^{2-}, Co Cr, Ti, Ni, Ci, V, F	Gabriëls *et al*. 1981
Lumogallion	Natural water	0.5	F, Fe (100 $\mu g \cdot L^{-1}$) organic matter	Hydes and Liss 1976

[α] Value in parentheses is the absolute detection limit.

[β] Cationic or nonionic surfactants strongly enhance fluorescence.

et al. (1978) reported a detection limit of 0.6 $\mu g.L^{-1}$ Al for aluminum solutions aspirated into a nitrous oxide - acetylene flame, and then analyzed by laser-excited fluorescence.

7.5.4.3 X-ray Fluorescence Spectrometry

In principle, X-ray fluorescence spectrometry may be used to perform simultaneous multielement analysis. When aluminum atoms are exposed to X rays of certain wavelength or to high-energy protons or electrons, they fluoresce by emitting X rays of characteristic wavelength. Because the fluorescence takes place in a thin layer at the sample surface, maximum sensitivity may be achieved by pretreating the sample so that the atoms of analytical interest are presented in a thin layer located within a well-defined surface area. For particles suspended in air or water this is done by simple filtration (Tanner et al. 1974). For aluminum in solution, the same effect can be achieved using filters impregnated with ion-exchange resins (Campbell et al. 1966). Absolute detection limits are generally in the microgram range for excitation with X rays but drop to the nanogram range when beams of accelerated charged particles (protons, alpha particles, etc.) are used as the excitation source (Cahill et al. 1971). The electron probe uses an intense narrow beam of highly accelerated electrons to excite X-ray fluorescence. The absolute detection limit for this method is in the order of 10^{-15} g (Baumgartl et al. 1973). Although the absolute detection limits quoted above are quite low, the relative detection limits all lie in the range 10-100 $mg \cdot kg^{-1}$ because of the small volume of analyte actually sampled by the X-ray fluorescence methods.

7.5.4.4 Electron Spectroscopy for Chemical Analysis (ESCA)

ESCA is similar in principle to X-ray fluorescence except that irradiation of a thin film of sample with X rays of known energy is used to eject electrons from the sample atoms. The electrons of each element have particular binding energies depending on their quantum level and, to a lesser extent, on the state of chemical binding of the atom in question. The measured energy of the ejected electron is equal to that of the exciting X ray minus the binding energy. Thus, in principle, it is possible to use ESCA for distinguishing the different chemical species of aluminum found in a sample. For example, Dillard et al. (1980) used ESCA to determine that rocket exhaust consisted of particulate matter containing, among other things, the following aluminum species: $AlCl_3$, Al_2O_3, $Al_2O_3 \cdot HCl$, and $Al_2O_3 \cdot H_2O$.

7.5.5 ACTIVATION ANALYSIS

Activation analysis involves bombarding the nucleus of an atom with neutrons or charged particles in order to elicit a reaction that yields either particles or electromagnetic radiation characteristic of the element in question. Because the reaction involves the nucleus, the chemical state of the element (which involves the outer-shell electrons) has no effect on the analytical signal, and activation analysis is, in this sense, free from matrix effects. Once the sample has been irradiated, contamination problems need not be considered, because any reagent blank will consist only of nonradioactive species that are not measured by the detector. However, interferences are still encountered: (i) from reactions that produce particles and electromagnetic radiation of identical or almost identical energy; or (ii) from elements that become so strongly activated that the background generated swamps out the analytical signal of the element sought.

7.5.5.1 Neutron Activation

All naturally occurring aluminum is present as the isotope ^{27}Al. This isotope accepts a neutron into its nucleus (with a reaction cross section (probability) of 0.23 x 10^{-24} cm^2) to form ^{28}Al (half life = 2.3 min; principal gamma energy = 1.779 MeV). Neutron activation requires a neutron source such as a nuclear reactor (Dams et al. 1971) or ^{252}Cf (John 1971), a radioactive isotope. The probability that a given atom of aluminum in the sample will be activated is proportional to the neutron density produced by the source (the flux). The probability that the characteristic radiation will be detected depends on the configuration and efficiency of the detector. These two factors largely determine the attainable detection limits listed in Table 7-12. As can be seen in the table, detection limits in the nanogram range are easily achieved where interferences are negligible (e.g., rocks, bone, airborne particles); however, especially in the case of biological samples containing sodium, potassium, chlorine, or bromine, chemical separation may be necessary to reduce the intense background produced by these elements. The difficulty with separations involving aluminum is that the short half-life of the radioactive product, 2.3 min, requires either a very rapid postirradiation procedure (see Buono et al. 1977) or careful control of contamination in a preirradiation procedure (see Blotcky et al. 1976). Thus, the method is not recommended for analysis of biological samples unless aluminum concentrations are moderately high. Phosphorus can interfere with aluminum determination because it is also converted to ^{28}Al, although at a much lower efficiency. This interference can be eliminated based on the phosphorus content of the sample and the activation intensity of phosphorus. It should be noted that pneumatic sample delivery systems of reactors are often made of the alloy AlMg$_3$. This requires that the sample be double-encapsulated to prevent aluminum contamination and/or transferred to nonirradiated vials before counting.

7.5.5.2 Charged-particle Activation Analysis

Bombarding ^{27}Al with protons, ^{3}He, etc., results in the emission of radiation with energies characteristic of aluminum. The source of charged particles is either a Van de Graaff accelerator or a cyclotron. The

Table 7-12. Determination of aluminum using neutron activation analysis.

Neutron energy	Matrix analyzed	Sample handling	Detection limit	Reference
Thermal	Airborne particles[α]	High volume filtration[β]; flux[γ] = 2 x 10^{13} for 5 min	1 ng·m^{-3} (50 ng)[δ]	Zoller and Gordon 1970
Thermal (^{252}Cf)	Natural waters[α]	Reverse osmosis	0.03 mg·L^{-1}	John 1971
Thermal	Oil shale products[α]	Fractionation by distillation; flux = 1 x 10^{14} for 3 min	0.6 mg·L^{-1}	Shaw *et al.* 1981
Thermal	Biological fluids, tissues	Sample dissolved; flux[γ] = 4 x 10^{12}, Al rapidly isolated	(0.2 μg)[δ]	Buono *et al.* 1977
Thermal	Urine, tissue	Preseparation onto cationic resin; flux[γ] = 3 x 10^{11}	0.05 mg·L^{-1}	Blotcky *et al.* 1976
Thermal	Estuarine suspended	Filter[ε]; flux[γ] = 10^{12}	(1 μg)[δ]	Ellis and Chattopadhyay 1979
Thermal and epithermal	Bone powder	Irradiation with and without Cd shield[ζ]	1 μg for [P]/[Al] = 2500	Gatschke and Gawlik 1980
14 MeV[η]	Air particulate	High-volume filtration	80 μg	Cercasov 1979

[α] Multielement method.

[β] The Millipore filter had an Al blank of 3.9 ng·cm^{-2} (or 0.1 μg Al per 57 diameter filter).

[γ] Flux measured in neutrons per square centimetre per second.

[δ] Absolute detection limit.

[ε] Nuclepore filters that were used contained 17 ng·cm^{-2} Al.

[ζ] Used to separate out ^{28}Al produced by reaction ^{31}P(n, α)^{28}Al.

[η] Reaction: ^{27}Al(n, p)^{27}Mg, interference: ^{30}Si(n, d)^{27}Mg.

advantage of these activation sources is that they may strongly activate the element of interest (e.g., Al), and only weakly activate the matrix elements (i.e., in certain cases they have a useful selectivity). Examples involving the determination of aluminum are given in Table 7-13. Unless the accelerator equipment and detectors are readily available, this method offers little advantage over other spectroscopic methods.

7.5.6 GAS CHROMATOGRAPHY (GC)

Metal chelates containing perfluoralkyl groups exhibit a high sensitivity in GC electron-capture detectors. This, coupled with the ability of some chromatographic columns to separate mixtures of chelated metals, provides the basis of an elegant micromethod for determining dissolved aluminum (Mushak 1977). Gosink (1975) reported the simultaneous determination of aluminum and chromium dissolved in water at levels as low as 0.6 $\mu g \cdot L^{-1}$ (absolute detection limit 1.2 x 10^{-12} g). Indium and gallium, two elements rarely found above trace levels in environmental samples, were identified as interferences.

7.5.7 ELECTROCHEMICAL METHODS

Although a number of electrochemical techniques have been used to determine aluminum, the most sensitive reported thus far is differential pulse polarography. Using this method (pH 4.0; KCl supporting electrolyte) it was possible to quantitatively determine aluminum in the concentration range 0.005-1.0 $ng \cdot L^{-1}$ Al (Ritchie et al. 1980). Only Na^+, NH_4^+, Mg^{2+}, and Ca^{2+} interfered, and only at concentrations 100 times greater than that of the aluminum.

7.5.8 MASS SPECTROMETRY

The use of mass spectrometers to determine a single element, such as aluminum, is not cost-effective. However, when the simultaneous-multielement capability of the instruments is used, the method becomes quite attractive, especially for large numbers of routine samples. The detection limits generally lie in the microgram per kilogram range. Tong et al. (1975) used spark-source mass spectrometry to simultaneously determine aluminum and 46 other elements in ashed samples of honey.

Another mass spectrometric technique involves mass spectrometric analysis of secondary ions sputtered from the sample surface using a high-energy beam of ions. Unlike most of the other methods mentioned thus far, this method may be used to determine the distribution and concentration of elements at the surface of a sample (Andersen and Hinthorne 1972). Some instruments provide an ion image of the sample (much like an electron

Table 7-13. Determination of aluminum using charged-particle activation analysis.

Activating particles	Matrix analyzed	Sample handling	Detection limit ($mg \cdot kg^{-1}$)	Reference
1.8 MeV protons[α]	Rock, plant	Pulverize, pelletize	100	Boulton and Ewan 1977
14 MeV ^3He[β]	High-purity metal foil	Irradiate at 2μA current for 2.3 min	0.017[γ]	Sastri *et al.* 1977
1-2 MeV protons[α]	Steel, rock, uranyl nitrate	-	10-100	Deconninck and Demortimer 1972

[α] $^{27}Al\ (p, p^1)^{27}Al$; protons accelerated by a Van de Graaff generator.

[β] $^{27}Al\ (^3He, 2p)^{28}Al$; ^3He accelerated using a cyclotron.

[γ] Interference-free detection limit; Mg would be expected to interfere: $^{26}Mg(^3He, p)^{28}Al$.

microscope image) where only those regions that yield a given ion are outlined (Galle and Lefevre 1978). Calibration materials are not readily available, and matrix effects are pronounced; however, valuable semiquantitative and even quantitative data have been produced using this technique (see Table 7-14).

7.6 STANDARD REFERENCE MATERIALS (SRM)

A number of agencies produce and distribute well-characterized calibration standards representing diverse matrices (see Abbey 1977 for a partial listing). Whereas numerous SRM with certified aluminum concentrations are available for geological and metallurgical matrices, few exist for environmental or biological matrices. At present, there are no standard reference materials for the analysis of trace ($<1\ \mathrm{mg \cdot kg^{-1}}$) aluminum in biological samples such as brain tissue. Some examples of SRM for aluminum in different matrices are listed in Table 7-15.

Carron and Aspila (1976) reported on an interlaboratory comparative analysis study on the determination of aluminum dissolved in both distilled and natural water at levels between 0.01 and 0.65 $\mathrm{mg \cdot L^{-1}}$ Al. The coefficient of variation ranged from 19 to 147% and increased with decreasing aluminum concentration. There was less agreement on the natural water samples than on distilled water.

7.7 CONCLUSION

Although a number of methods (AA, AES, X-ray fluorescence, mass spectrometry, and neutron activation) are suitable for determining the percent levels of aluminum in geological and metallurgical samples, only a few methods (AA, AES, and GC-electron capture) excel when aluminum must be determined in biological tissues.

Table 7-14. Ion probe analysis for aluminum.

Matrix	Data acquired	Comment	Reference
Geological (mineral standards)	Quantitative analysis of percent levels		Andersen and Hinthorne 1972
Geological and metallurgical	Quantitative analysis	Successful analysis in silicate but high results for metals	Andersen and Hinthorne 1972
Fly ash	Al concentration vs. depth from particle surface (qualitative)	Al level was 1%; Al not concentrated at surface	Linton _et_ _al_. 1977
Tissue-thin sections	Qualitative	Al accumulated in cell nuclei	Truchet 1976
Human sperm	Qualitative	Al from wash water not intrinsic	Galle and Lefevre 1978
Steel, semiconductors	Quantitative	Accuracy 15-50%	Leta and Morrison 1980

Table 7-15. Some examples of standard reference materials (SRM) with a certified aluminum concentration.

Matrix	SRM	Supplier	Catalogue No.	Al concentration
Geological	Marine sediment	NRCC[α]	MESS-1	11.03% (Al_2O_3)
	Marine sediment	NRCC[α]	BCSS-1	11.83% (Al_2O_3)
	Andesite	USGS[β]	AGV-1	17.22% (Al_2O_3)
	Dunite	USGS[β]	DTS-1	0.29% (Al_2O_3)
Metallurgical	Low-alloy steel	NBS[γ]	179	28 $mg \cdot kg^{-1}$ (Al)
	Low-alloy steel	NBS[γ]	661	210 $mg \cdot kg^{-1}$ (Al)
Biological	Spinach	NBS[γ]	1570	870 $mg \cdot kg^{-1}$ (Al)
	Pine needles	NBS[γ]	1575	545 $mg \cdot kg^{-1}$ (Al)
Environmental	Bituminous coal	NBS[γ]	1632a	1.64% (Al)

[α] National Research Council of Canada, Division of Chemistry, Marine Analytical Chemistry Standards Program, Ottawa, Canada K1A 0R6.

[β] U.S. Geological Survey, U.S. Dep. of Interior, Reston, Virginia, U.S.A. 22092.

[γ] U.S. National Bureau of Standards, Office of Standard Reference Materials, Gaithersbury, Maryland, U.S.A. 20234.

APPENDIX I.0

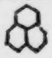
Aluminum Hydrolysis Review

APPENDIX I.0

Aluminum Hydrolysis Review

The first hydrolysis complex of Al^{3+}, well documented by over 20 references, shows differences in the K_1 value by more than one order of magnitude. For the same ionic medium, ionic strength, and temperature, the reported values of the pK range between 4.75 (Hem and Roberson 1967) and 5.27 (Kubota 1956). Often the value for the first hydrolysis constant is 5.00 ± 0.05 for 25°C, ionic strength ≤ 0.03, and a total aluminum concentration of 0.01 M and less (Schofield and Taylor 1954; Raupach 1963; May et al. 1979b).

The disagreement is much worse with the other hydrolysis products. There is a major problem specifying the stoichiometry and stability constant for the polynuclear complexes. In particular, there is a large variation in the pK values. For example, the pK value of the $Al_6(OH)_{15}^{3+}$ complex, which is reported by several authors and which could be a unit of the Gibbsite structure, varies by nine orders of magnitude.

$Al_6(OH)_{15}^{3+}$, $Al_{13}(OH)_{32}^{7+}$, and $Al_8(OH)_{20}^{4+}$ species have been proposed. The $Al_6(OH)_{15}^{3+}$ complex is a unit of the Gibbsite structure , and the $Al_{13}(OH)_{32}^{7+}$ could be a multiple of the unit .

In summary, the following complexes may best define the hydrolysis of Al^{3+}:

$Al(OH)^{2+}$	pβ	5.0	Kubota 1956; Raupach 1957; May et al. 1979
$Al(OH)_4^-$	pβ	23.7	Reesman et al. 1969; Hayden and Rubin 1974
$Al_6(OH)_{15}^{3+}$	pβ	47.0	Brosset et al. 1954
$Al_{13}(OH)_{32}^{7+}$	pβ	104.5	Aveston 1965

$$\text{where } \beta_{i,j} = \frac{[Al_i\ (OH)_j^{(3i-j)}]\ [H^+]^j}{[Al^{3+}]^i}.$$

Table I-1.

Species	pK	Ionic medium and strength	Temp. (°C)	Al_{tot}	Method of determination	Reference
$AlOH^{2+}$	5.35	0.4	25	0.05 M	Potentiometry	De Hek et al. 1978
	4.89	0.1 M $NaClO_4$	25	0.01 M	Spectrophotometry - competing ligands	Nazarenko and Nevskaya 1969
	4.90	0.1 M $NaClO_4$	25	0.01 M	Spectrophotometry: Alizarin 3S	Nazarenko and Biryuk 1974
	5.04	(0)	25	0.01 M	"	Nazarenko and Biryuk 1974
	4.60	0.3 M $NaClO_4$	25	0.01 M	"	Nazarenko and Biryuk 1974
	4.30	0.5 M $NaClO_4$	25	0.01 M	"	Nazarenko and Biryuk 1974
	3.60	1.0 M $NaClO_4$	25	0.01 M	"	Nazarenko and Biryuk 1974
	4.61	0.1-0.5	30	0.06-0.007	Potentiometry	Grunwald and Fong 1969
	5.05	0.03	25	10^{-2}-$3x10^{-5}$	Conductivity measurements	Raupach 1963
	5.00	0.03	25	10^{-2}-$3x10^{-5}$	Potentiometry	Raupach 1963
	4.98	0.001 KCl(0)	25	10^{-2}-$5x10^{-5}$	Potentiometry (glass electrode)	Schofield and Taylor 1954
	4.89	(0)	15	10^{-2}-10^{-4}	pH measurements (catalytic diazoacetic ester method)	Bronsted and Volqvartz 1928
	5.55	0.15 M $NaNO_3$	25	10^{-2}-$5x10^{-5}$	Potentiometry, light scattering	Hayden and Rubin 1974
	5.02	(0)	25	10^{-2}-10^{-6}	Potentiometry, conductivity	Frink and Peech 1963a
	5.44	1 M KNO_3	25	2.7-10^{-3}	Potentiometry (glass electrode)	Pulfer 1981
	4.96	(0)	25	≥0.001	"	Hartford 1942
	5.97	0.6 NO_3^-	20	<$5x10^{-3}$	"	Faucherre 1954
	5.74	0.12 NO_3^-	20	<$5x10^{-3}$	"	Faucherre 1954
	5.27	0.01 $NaClO_4$	25	0.001	"	Kubota 1956
	5.03	(0)	25	0.001	"	Kubota 1956
	4.93	0.001 ClO_4^-	25	0.001	"	Kubota 1956
	5.29	0.0001 ClO_4^-	25	0.0001	"	Sullivan and Singley 1968
	4.75	0.01 M $NaClO_4$	25	10^{-4}-10^{-5}	"	Hem and Roberson 1967
	4.89	10^{-4}-2.8 $NaNO_3$,NaCl	25	$5x10^{-5}$	Potentiometry	Stol et al. 1976
	5.16	10^{-5} ClO_4^-	25	10^{-6}	"	Sullivan and Singley 1968
	4.99	0.01 M $NaNO_3$	25	$2x10^{-6}$-$14x10^{-5}$	Potentiometry, spectrophotometry	May et al. 1979b
	5.01	(0)	25	Literature research, average (Raupach 1963; Schofield and Taylor 1954; Frink and Peech 1963a)		Parks 1972

Table I-1. (Cont'd)

Species	pK	Ionic medium and strength	Temp. (°C)	Al_{tot}	Method of determination	Reference
$AlOH^{2+}$	5.01	(0)	25	Monomeric model, values from Parks 1972		Marion et al. 1976
	5.10	nr$^{\alpha}$	25	nr	pH measurements, conductivity	Ito and Yui 1953
	4.96	nr	25	nr	pH measurements, cryoscopy	Kenttamaa 1955
	5.47	1 M $NaClO_4$	25	nr		Mesmer and Baes 1971
	5.52	0.5	25	nr		Smith and Martell 1976
	5.69	1.0	25	nr		Smith and Martell 1976
	4.99	(0)	25	nr		Smith and Martell 1976
$Al(OH)_2^+$	10.40	0.1 M $NaClO_4$	25	$2.7x10^{-2}-3x10^{-4}$	Potentiometry (glass electrode)	Reesman et al. 1969
	10.65	(0)	25	0.01	Spectrophotometry	Nazarenko and Biryuk 1974
	10.35	0.1	25	0.01	"	Nazarenko and Biryuk 1974
	9.73	0.3	25	0.01	"	Nazarenko and Biryuk 1974
	9.12	0.5	25	0.01	"	Nazarenko and Biryuk 1974
	7.58	1.0	25	0.01	"	Nazarenko and Biryuk 1974
	9.76	0.03	25	$10^{-2}-3x10^{-5}$	Potentiometry	Raupach 1963
	10.59	1 M KNO_3	25	$2x10^{-3}$	Potentiometry (glass electrode)	Pulfer 1981
	9.96	0.001 ClO_4^-	25	0.001	Potentiometry	Sullivan and Singley 1968
	10.59	0.0001 ClO_4^-	25	0.0001	"	Sullivan and Singley 1968
	10.32	$2.8-10^{-4}$ $NaCl,NO_3^-$	25	$10x10^{-5}$	"	Stol et al. 1976
	10.3	0.1 M $NaClO_4$	25	$2x10^{-5}$	Spectrophotometry, competing ligands	Nazarenko and Nevskaya 1969
	11	(0)	25	10^{-5}	Potentiometry	Frink and Peech 1963a
	12.12	10^{-5} ClO_4^-	25	10^{-5}	"	Sullivan and Singley 1968
	8.70	0.1 M	25	Literature review		Parks 1972
	8.70	(0)	25	Value from Parks 1972		Marion et al. 1976
	9.70	Theoretical treatment of data from Raupach 1963				Turner 1968

Table I-1. (Cont'd)

Species	pK	Ionic medium and strength	Temp. (°C)	Al_{tot}	Method of determination	Reference
$AlOH_2^+$	8.67	nr	25	nr		Hemingway *et al.* 1978
	10.40	0.5	25	nr	nr	Smith and Martell 1976
	9.30	(0)	25	nr	nr	Smith and Martell 1976
$Al(OH)_3$	15.32	0.6 M NaCl	20	0.2-0.03	Potentiometry (glass electrode)	Dezelic *et al.* 1971
	16.75	(0)	25	0.01	Spectrophotometry	Nazarenko and Biryuk 1974
	16.25	0.1	25	0.01	"	Nazarenko and Biryuk 1974
	15.25	0.3	25	0.01	"	Nazarenko and Biryuk 1974
	14.38	0.5	25	0.01	"	Nazarenko and Biryuk 1974
	11.84	1.0	25	0.01	"	Nazarenko and Biryuk 1974
	15.93	1 M KNO_3	25	0.002	Potentiometry (glass electrode)	Pulfer 1981
	14.13	0.001 ClO_4^-	25	0.001	"	Sullivan and Singley 1968
	15.19	0.0001 ClO_4^-	25	0.0001	"	Sullivan and Singley 1968
	16.28	$2.8 \cdot 10^{-4}$ $NaNO_3$,NaCl	25	$5x10^{-5}$	"	Stol *et al.* 1976
	15.6	0.1 M $NaClO_4$	25	$2x10^{-5}$	Spectrophotometry	Nazarenko and Nevskaya 1969
	23.49	10^{-5} ClO_4^-	25	10^{-5}	Potentiometry	Sullivan and Singley 1968
	15.20	0.1	25	Literature research		Parks 1972
	15.20	0.1	25	Value from Parks 1972		Marion *et al.* 1976
	13.02	Calculated from literature data				Dalal 1975
	16.30	0.5	25	nr	nr	Smith and Martell 1976
	15.00	(0)	25	nr	nr	Smith and Martell 1976
$Al(OH)_4^-$	21.47	1-0.01 M $AlCl_3$	20	1-0.01	Potentiometry	LaCroix 1949
	23.75	0.15 M $NaNO_3$	25	$5x10^{-2}-5x10^{-5}$	Analysis of precipitation boundaries	Hayden and Rubin 1974
	23.23	nr	20	0.04-0.002	Potentiometry (Sb electrode)	Szabo *et al.* 1955
	23.74	0.01 M $NaClO_4$	25	0.03-0.003	Potentiometry (glass electrode)	Reesman *et al.* 1969
	23.55	0.001 ClO_4	25	0.001	Potentiometry	Sullivan and Singley 1968
	23.93	0.0014-0.0044	23-25	$2.8x10^{-4}-10^{-4}$	Potentiometry (glass electrode)	Kittrick 1966
	23.30	0.0001 ClO_4^-	25	0.0001	Potentiometry	Sullivan and Singley 1968
	23.30	0.0001 ClO_4^-	25	0.0001	Value from Parks 1972	Marion *et al.* 1976

Table I-1. (Cont'd)

Species	pK	Ionic medium and strength	Temp. (°C)	Al_{tot}	Method of determination	Reference
$Al(OH)_4^-$	22.73	0.01 M $NaClO_4$	25	$10^{-4}-10^{-5}$	Potentiometry	Hem and Roberson 1967
	22.17	0.01 M $NaClO_4$	25	$1.4x10^{-5}-2x10^{-8}$	"	May et al. 1979b
	31.46	10^{-5} ClO_4^-	25	10^{-5}	"	Sullivan and Singley 1968
	23.57					Bolt and Bruggenwert 1976
	23.29		25			Hemingway et al. 1978
	23.30	Literature review				Parks 1972
	22.93					Oka 1938
$Al(OH)_5^{2-}$	34.95	0.001	25	10^{-3}	Potentiometry	Sullivan and Singley 1968
	34.06	10^{-4}	25	10^{-4}	Value from Sullivan and Singley 1968	Marion et al. 1976
	34.06	10^{-4}	25	10^{-4}	Potentiometry	Sullivan and Singley 1968
	40.32	10^{-8}	25	10^{-5}	"	Sullivan and Singley 1968
$Al_2(OH)_2^{4-}$	7.07	1 M $NaClO_4$	25	0.1-0.003	Potentiometry	Aveston 1965
	6.37	0.06	30	0.06	"	Grunwald and Fong 1967
	7.1	0.4	25	0.05	Potentiometry	Hayden and Rubin 1974
	8.23	0.6	20	10^{-2}	"	Faucherre 1954
	8.06	0.12	20	10^{-2}	"	Faucherre 1954
	7.42	0.06	25	$10^{-2}-10^{-4}$	"	Turner 1975
	6.95	(0)	25	$10^{-2}-10^{-4}$	"	Turner 1975
	7.5	0.007	30	0.007	"	Grunwald and Fong 1969
	7.7	1 M KCl	62.5	0.005	Potentiometry (H_2-electrode)	Mesmer and Baes 1971
	6.23	(0)	25	10^{-3}	Potentiometry, conductivity	Frink and Peech 1963a
	6.22	(0)	25			Kubota 1956
	7.55	nr	25	nr	Potentiometry, cryoscopy	Kenttamaa 1955
$Al_3(OH)_4^{5+}$	nr	1 M KCl	124.8	0.05	Potentiometry (H_2-electrode)	Mesmer and Baes 1971
$Al_3(OH)_8^+$	only evidence of existence				IR (infrared)	Tanabe 1954 Raupach 1957

Table I-1. (Cont'd)

Species	pK	Ionic medium and strength	Temp. (°C)	Al_{tot}	Method of determination	Reference
$Al_4(OH)_8^{4+}$	nr	2 M $NaNO_3$	30	0.01	Potentiometry	Fripiat *et al.* 1965
	27	2 M $NaNO_3$	30	0.04-0.005	Potentiometry (glass electrode)	Van Cauwelaert and Bosmans 1969
	25.5	2 M $NaNO_3$	40	0.04-0.0003	"	Van Cauwelaert and Bosmans 1969
$Al_4(OH)_{10}^{2+}$	nr	nr	25	nr	Potentiometry, cryoscopy	Kenttamaa 1955
$Al_6(OH)_{12}^{6+}$		Theoretical considerations				Hsu and Bates 1964b
$Al_6(OH)_{13}^{5+}$						Gresky *et al.* 1960
$Al_6(OH)_{15}^{3+}$	47	2 M $NaClO_4$	40	10^{-2}	Careful analysis of earlier data	Brosset *et al.* 1954
	35.9	(0)	25	10^{-3}	Numeric treatment of literature data	Nair and Prenzel 1978
$Al_7(OH)_{16}^{5+}$		2 M $NaNO_3$		10^{-2}	Potentiometry	Fripiat *et al.* 1965
	52.7	2 M $NaNO_3$	30	0.04-0.005	Potentiometry (glass electrode)	Van Cauwelaert and Bosmans 1969
	48.5	2 M $NaNO_3$	40	0.04-0.0003	"	Van Cauwelaert and Bosmans 1969
$Al_7(OH)_{17}^{4+}$	48.80	3 M $NaClO_4$	25		Potentiometry	Sillén and Martell 1971
	36	(0)	25	10^{-3}	Numeric treatment of literature data	Nair and Prenzel 1978
$Al_8(OH)_{20}^{4+}$	68.65	0.15 $NaNO_3$	25	10^{-3}-10^{-4}	Potentiometry, light scattering	Hayden and Rubin 1974
	nr	nr	nr	$7x10^{-6}$	Coagulation studies	Matijevic *et al.* 1961
$Al_8(OH)_{22}^{2+}$	nr	nr	nr	$7x10^{-6}$	"	Matijevic *et al.* 1961
$Al_8(OH)_{24}$	nr	nr	nr	$7x10^{-6}$	"	Matijevic *et al.* 1961
$Al_{10}(OH)_{22}^{8+}$	nr	nr	nr	0.001	Precipitation studies	Hsu 1977

Table I-1. (Cont'd)

Species	pK	Ionic medium and strength	Temp. (°C)	Al_{tot}	Method of determination	Reference
$Al_{10}(OH)_{24}^{6+}$	nr	2 M $NaNO_3$	30,40	0.04–0.0003	Potentiometry	Van Cauwelaert and Bosmans 1969
$Al_{13}(OH)_{32}^{7+}$	104.5	1 M $NaClO_4$	25		Potentiometry, ultracentrifugation	Aveston 1965
	80.66	(0)	25	10^{-3}		Nair and Prenzel 1978
	nr	2 M $NaNO_3$	30,40	0.04–0.0003	Potentiometry	Van Cauwelaert and Bosmans 1969 Sillén 1959
$Al_{13}(OH)_{34}^{5+}$	97.60	3 M $NaClO_4$	25		Potentiometry	Sillén and Martell 1971
	73.3	(0)	25	10^{-3}	Numeric treatment of literature data	Nair and Prenzel 1978
$[Al_{13}O_4(OH)_{24}(OH_2)_{12}]^{7+}$	nr	nr	nr	0.5	^{27}Al NMR	Akitt and Farthing 1981
	nr	nr	70	1	Precipitation studies $Al(NO_3)_3$ with Na_2CO_3	Rausch and Bale 1964

[a] nr = not reported.

APPENDIX II.0

Aluminum-Organic Speciation

APPENDIX II.0

Aluminum-Organic Speciation

Data abound for the dissociation constants of the organic acids. There is even good agreement for the more common ones. But there are data for only a few aluminum-organic constants. The constants in the tables are defined for the following equilibria unless otherwise noted:

$$HA + H_2O = H_3O^+ + A^-$$

$$\text{thus } K_a = \frac{[H^+]\,[A^-]}{[HA]} \text{ etc.}$$

and for the complex formation:

$$M + L_i = ML_i$$

$$\beta_i = \frac{[ML_i]}{[M]\,[L]^i}$$

Care must be taken in using the complex formation constants for calculations, because most of them are conditional stability constants, determined under very acidic conditions (i.e., pH 1.65-3.5). Havelkova and Bartusek (1969) determined their constants by titrating the aluminum solution containing the ligands from pH 3 up to pH 8 (formation of aluminum hydroxide).

Table II-1. Formic acid (HCOOH).

Temp. (°C)	Ionic medium/ strength	$-\log K_a$	Reference
25	0.1 M KCl	3.739	161
31	0.1 M $NaClO_4$	3.54	154
18	0.01	3.747	99
25	0.004	3.760 ± 0.005	182
25	0.4	3.55	104
30	0.4	3.53 ± 0.03	31
20	1 M $NaClO_4$	3.56	144
20	1 M $NaClO_4$	3.49	139
25	1 M $NaClO_4$	3.53	86
25	1 M $NaNO_3$	3.43	91
25	3 M $NaClO_4$	3.900 ± 0.005	144
25	3 M KCl	3.84 ± 0.02	73
25	5 M $NaClO_4$	4.39 ± 0.02	73
25	0.0	3.75	78
25	0.0	3.751	15
25	0.0	3.75	61
25	0.0	3.752	40
25	0.0	3.739 ± 0.001	146
25	0.0	3.737 ± 0.01	19
25	0.0	3.751	39
25	0.0	3.77	33
25	0.0	3.75	53
		$\log \beta$	
25	1 M $NaNO_3$	1.36 ± 0.03	91

Table II-2. Acetic acid (CH_3-COOH).

Temp. (°C)	Ionic medium/ strength	-log K	Reference
25	0.004	4.754 ± 0.010	182
18	0.01	4.761	98
18	0.01	4.761	99
25	0.1	4.61	183
25	0.1 M KCl	4.56 ± 0.02	11
25	0.1	4.53	187
20	0.1 M $NaClO_4$	4.55	96
25	0.1 M KCl	4.559	27
25	0.1 M KCl	4.562	90
25	0.1	4.59	167
20	0.1 M $NaNO_3$	ΔH = -0.280 ± 0.005	165
25(?)	0.2	4.640	34
25	0.2 M KCl	4.67	46
25	0.4	4.65	104
30	0.4	4.56 ± 0.03	31
25	0.5 M $LiClO_4$	4.48 ± 0.03	46
25	0.51	4.475	80
20	1 M $NaClO_4$	4.59	144
20	1 M $NaClO_4$	4.59	5
20	1 M $NaClO_4$	4.55	139
25	1 M $NaNO_3$	4.54	91
25	1.01	4.4957	80
25	2 M $NaClO_4$	4.74	59
25	2 M $NaClO_4$	4.80	38
25	2.01	4.5875	80
25	3 M $NaClO_4$	5.014 ± 0.009	114
25	3 M $NaClO_4$	4.985 ± 0.006	64
25	3 M $NaClO_4$	5.02 ± 0.01	37
25	3 M $NaClO_4$	4.985 ± 0.001	141
25	3 M $NaClO_4$	5.015 ± 0.010	65
25	3.01	4.7132	80
25	0.0	4.7565	15
25	0.0	4.756	40
25	0.0	4.756	93
25	0.0	4.766	39
25	0.0	4.7584	147
25	0.0	4.756	9
25	0.0	4.75	112
25	0.0	4.758 ± 0.005	107
25	0.0	4.756	108
25	0.0	4.756	76
25	0.0	4.755	162

Table II-2. (Cont'd)

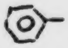
Temp. (°C)	Ionic medium/ strength	-log K	Reference
25	0.0	4.754	80
25	0.0	4.76	10
25	0.0	4.756	54
25	0.0	4.75	47
25	0.0	4.76	33
25	0.0	4.76	18
25	0.0	4.76	53
		log β	
25	1 M $NaNO_3$	1.50 ± 0.04	91

Table II-3. Propanoic acid (propionic acid) (C_2H_5-COOH).

Temp. (°C)	Ionic medium/ strength	-log K	Reference
18	0.01	4.878	99
31	0.1 M $NaClO_4$	4.62	154
20	0.1 M $NaClO_4$	4.67	145
25	0.1 M KCl	4.69	159
25(?)	0.2	4.703	34
25	0.4	4.80	104
20	1 M $NaClO_4$	4.73	144
20	1 M $NaClO_4$	4.66	139
25	1 M $NaNO_3$	4.56	91
25	2 M $NaClO_4$	4.89	59
25	3 M $NaClO_4$	5.161 ± 0.006	114
25	0.0	4.874	40
25	0.0	4.874	39
25	0.0	4.874	77
25	0.0	4.87	71
25	0.0	4.89	159
25	0.0	4.875	54
25	0.0	4.88	33
25	0.0	4.87	53
		log β	
25	1 M $NaNO_3$	1.69 ± 0.06	91

Table II-4. Butanoic acid (butyric acid) (C_3H_7COOH).

Temp. (°C)	Ionic medium/ strength	-log K	Reference
18	0.01	4.816	99
25	0.1 M Kcl	4.819	161
31	0.1 M $NaClO_4$	4.63	153
25(?)	0.2	4.742	34
20	1 M $NaClO_4$	4.69	144
25	1 M $NaNO_3$	4.57	91
25	2 M $NaClO_4$	4.86	59
25	3 M $NaClO_4$	5.132 ± 0.007	114
25	0.0	4.817	40
25	0.0	4.820	39
25	0.0	4.82	79
25	0.0	4.82	54
25	0.0	4.82	43
25	0.0	4.82	33
25	0.0	4.82	53
		log β	
25	1 M $NaNO_3$	1.58 ± 0.04	91

Table II-5. Benzoic acid ( COOH).

Temp. (°C)	Ionic medium/ strength	-log K	Reference
20	0.004	4.200 ± 0.005	182
31	0.1 M $NaClO_4$	4.01	154
25	0.1	4.01	187
25	0.1 M KCl	4.010	27
25	0.1	4.115 ± 0.002	28
30	0.4	3.97 ± 0.04	31
25	0.5 M $NaClO_4$	3.99 ± 0.02	126
25	0.0	4.20	92
25	0.0	4.201	39
25	0.0	4.20	30
25	0.0	4.20	163
25	0.0	4.20	22
25	0.0	4.19	10
25	0.0	4.21	43
25	0.0	4.19	47
25	0.0	4.2050 ± 0.0015	95
25	0.0	4.202	185
25	0.0	4.201 ± 0.004	105
25	0.0	4.14	56
25	0.0	4.204	116
25	0.0	4.201	89
25	0.0	4.202	49
25	0.0	4.21	33
25	0.0	4.203	157
25	0.0	4.20	60
25	0.0	4.21	128
25	0.0	4.202	177
25	0.0	4.21	158
rt	0.0	4.216	100
25	0.0	4.17	53
		log β	
25	0.5 M $NaClO_4$ for $Al^{3+} + B^- + OH^- = Al\ OHB^+$	12.09	126

Table II-6. Nitroacetic acid (O_2NCH_2COOH).

Temp. (°C)	Ionic medium/ strength	-log K	Reference
18	0.0	1.68	136
18	0.1	1.46	136
18	0.2 M $Ba(NO_3)_2$	1.34	137
		log β	
18	0.1 M $Ba(NO_3)_2$	0.48	137

Table II-7. Oxalic acid ($\begin{matrix}\mathrm{COOH}\\ | \\ \mathrm{COOH}\end{matrix}$).

Temp. (°C)	Ionic medium/ strength	$-\log K_{a_1}$	$-\log K_{a_2}$	Reference
25	0.1 M KNO_3	1.04	3.78	62
25	0.1 M KNO_3	1.26 ± 0.05	3.82 ± 0.01	42
25	0.1 M $NaClO_4$	1.13	3.85	125
25	0.1 M KNO_3	1.3	3.81 ± 0.01	102
20	0.11	1.05	3.92	181
25	0.15 M $NaClO_4$	1.33	3.59	44
25	0.2 M KCl	1.14	3.85	46
25(?)	0.2	1.14	3.85	34
25	0.5 M $LiClO_4$	1.00 ± 0.05	3.50 ± 0.03	46
25	0.5	1.20 ± 0.01	3.67 ± 0.1	17
25	1.0	1.08	3.55	121
20	1 M $NaClO_4$	1.00 ± 0.01	3.55	68
25	1 M KNO_3	1.1	3.62 ± 0.01	152
25	1 M $NaClO_4$	1.07 ± 0.05	3.57 ± 0.02	23
25	1 M $NaClO_4$	1.07 ± 0.05	3.57 ± 0.02	189
25	1 M $NaClO_4$	1.07	3.57	24
25	3	1.26	3.80	121
25	?	1.0	3.54 ± 0.01	164
25	0.0	1.271	4.266	39
25	0.0		4.286	82
25	0.0		4.266	142
25	0.0	1.36 ± 0.10	4.27 ± 0.02	180
25	0.0	1.27	4.3	109
25	0.0	1.36 ± 0.11		179
25	0.0	1.25		110

		$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	
25	1 M $NaClO_4$	6.06 ± 0.1	11.09 ± 0.05	15.12 ± 0.07	24

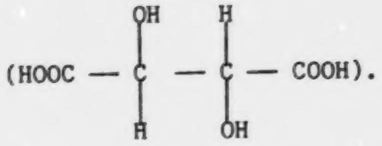
Table II-8. Oxidiacetic acid (diglycolic acid) ($HOOC-CH_2-O-CH_2-COOH$).

Temp. (°C)	Ionic medium/ strength	$-\log K_{a_1}$	$-\log K_{a_2}$	Reference
25	0.1 M KNO_3	2.73	3.92	119
25	0.1	2.77	3.92	187
25	0.1 M KNO_3	2.78 ± 0.01	3.95 ± 0.01	58
30	0.1 M KCl	2.90	4.03	173
31	0.1 M $NaClO_4$	2.77	3.88	154
25(?)	0.2		3.712	34
25	0.5 M $NaClO_4$	2.80 ± 0.01	3.76 ± 0.01	127
20	1 M $NaClO_4$	2.82 ± 0.02	3.75 ± 0.02	35
20	1 M $NaClO_4$	2.80	3.74	67
20	1 M $NaClO_4$	2.83	3.75	70
25	1 M $NaClO_4$	2.69	3.76 ± 0.04	69
25	2 M $NaClO_4$	2.91 ± 0.01	3.97 ± 0.02	8
25	0.0		3.84	94
25	0.0		3.831	27
25	0.0	2.967	4.368	168
25	0.0		3.83	53
		$\log \beta_1$	$\log \beta_2$	
25	0.5 M $NaClO_4$	3.16 ± 0.012	5.25 ± 0.02	127

Table II-9. Thiodiacetic acid (thiodiglycolic acid) (HOOC-CH$_2$-S-CH$_2$-OOH).

Temp. (°C)	Ionic medium/ strength	$-\log K_{a_1}$	$-\log K_{a_2}$	Reference
18	0.1 M NaCl	3.120	4.117	1
25	0.1 M NaClO$_4$	3.13 ± 0.05	4.14 ± 0.03	143
25	0.1 M KCl	3.09 ± 0.04	4.12 ± 0.04	143
25	0.1	3.15	4.13	187
30	0.1 M KCl	3.26	4.29	173
25	0.5 M NaClO$_4$	3.10 ± 0.01	4.03 ± 0.01	127
18	1 M NaCl	3.047	3.928	1
20	1 M NaClO$_4$	3.14 ± 0.02	4.04 ± 0.02	35
25	1 M NaClO$_4$	3.13	3.99	45
25	2 M NaClO$_4$	3.22 ± 0.01	4.14 ± 0.04	8
25	0.0	3.244	4.556	168
		$\log \beta_1$	$\log \beta_{11}$	
25	0.5 M NaClO$_4$	1.93 ± 0.08	12.34 ± 0.05	127

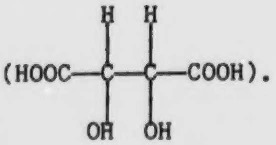
$\log \beta_{11}$ for $Al^{3+} + OH^- + TDA^{2-} \rightleftharpoons Al\ OH\ TDA$

Table II-10. D-Tartaric acid 

$$(\text{HOOC} - \underset{\text{H}}{\overset{\text{OH}}{\text{C}}} - \underset{\text{OH}}{\overset{\text{H}}{\text{C}}} - \text{COOH}).$$

Temp. (°C)	Ionic medium/ strength	$-\log K_{a_1}$	$-\log K_{a_2}$	Reference
20	0.1 M $NaClO_4$	2.83	4.02	6
20	0.1 M $NaClO_4$	2.80 ± 0.03	3.96 ± 0.02	175
25	0.1 M $NaClO_4$	2.73	3.78	155
25	0.1 M $NaClO_4$	2.73	3.78	156
25	0.1 M $NaClO_4$	2.73	3.78	113
25	0.1	2.83	3.97	50
25	0.133	2.81 ± 0.04	3.95 ± 0.02	55
25(?)	0.2	2.88	3.94	34
25	0.5	2.62	3.67	63
25	1 M $NaClO_4$	2.59 ± 0.02	3.84 ± 0.03	25
25	1 M KNO_3	2.60	3.77	190
25	0.0	3.04 ± 0.02	4.37	148
25	0.0	3.036	4.366	16
		$\log \beta_1$	$\log \beta_2$	
25	0.1 M $NaClO_4$	5.32	9.77	113

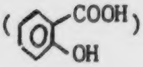
Table II-11. Meso-tartaric acid



$(HOOC{-}\underset{OH}{\overset{H}{C}}{-}\underset{OH}{\overset{H}{C}}{-}COOH)$.

Temp. (°C)	Ionic medium/ strength	$-\log K_{a_1}$	$-\log K_{a_2}$	Reference
20	0.1 M $NaClO_4$	3.16	4.55	6
25	0.1 M $NaClO_4$	2.84	4.23	155
25	0.1 M $NaClO_4$	2.84	4.23	156
25	0.1 M $NaClO_4$	2.84	4.23	113
25	0.1	2.90	4.11	167
25	0.133	2.99 ± 0.02	4.44 ± 0.03	55
25	1.5	2.90	4.12	66
25	0.0	3.04	4.31	39
25	0.0	3.23 ± 0.01	4.89	148
25	0.0	2.90	4.12	66
25	0.0	3.03	4.37	149
25	0.0	3.036	4.366	191
		$\log \beta_1$	$\log \beta_2$	
25	0.1 M $NaClO_4$	5.62	9.95	113

Table II-12. 2-Hydroxybenzoic acid (salicylic acid) (

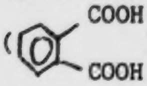


).

Temp. (°C)	Ionic medium/ strength	$-\log K_{a_1}$	$-\log K_{a_2}$	Reference
20	0.1 M KNO$_3$	2.92	13.1	188
20	0.1 M KNO$_3$		13.6	102
20	0.1 M KNO$_3$	2.92	13.1	84
25	0.1 M NaClO$_4$	2.87	13.40	156
25	0.1 M KNO$_3$	2.70 ± 0.02	13.90 ± 0.10	120
25	0.1 M KNO$_3$	2.80 ± 0.01	13.6	42
25	0.1 M KNO$_3$	2.89	13.6	97
25	0.1 M KNO$_3$	2.88 ± 0.02		102
25	0.1 M NaClO$_4$	2.82 ± 0.00		132
30	0.1 M KNO$_3$	2.99 ± 0.02	13.60	166
20	0.1-0.15	2.98	13.61	138
25	0.15 M NaClO$_4$	2.92	13.4	44
37	0.15 M KNO$_3$	2.814	13.0	140
25	0.17 M NaClO$_4$	2.820		27
25	0.5 M NaClO$_4$	2.82		111
25	3 M NaClO$_4$		13.12 ± 0.05	4
25	3 M NaClO$_4$	3.183 ± 0.014	13.12 ± 0.05	135
25	3 M NaClO$_4$	3.86 ± 0.01		3
25	3 M NaClO$_4$	3.173 ± 0.001		101
25	0.0	2.97	13.74	48
25	0.0	2.97	13.59	51
25	0.0	2.973		39
25	0.0	2.97		18
25	0.0	2.97		53
rt	0.0	3.026		100

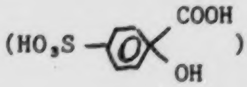
		$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	
20	0.1 M KNO$_3$	12.9	23.2	29.8	84

Table II-13. 1,2-Benzene dicarboxylic acid (phthalic acid)

().

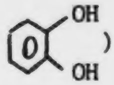
Temp. (°C)	Ionic medium/ strength	-log K_{a_1}	-log K_{a_2}	Reference
25	0.1	2.76	4.92	187
25	0.1 M $NaClO_4$	2.728	4.928	106
25	0.1 M KNO_3	2.76	4.92	186
30	0.1 M KNO_3	2.89 ± 0.02	5.04 ± 0.01	166
25	0.15 M $NaClO_4$	2.91	5.13	44
25	0.5 M $NaClO_4$	2.66 ± 0.02	4.74 ± 0.02	126
25	1 M KNO_3	2.63 ± 0.01	4.73 ± 0.01	152
25	3 M $NaClO_4$	3.05	4.89	131
25	0.0	2.95	5.42	39
25	0.0		5.4083 · 0.0008	74
25	0.0	2.9496 ± 0.0005		75
		log β_1	log β_2	
25	0.5 M $NaClO_4$	3.18 ± 0.03	6.32 ± 0.03	126

Table II-14. 2-Hydroxy-5-sulfobenzoic acid (5-sulfosalicylic acid)

().

Temp. (°C)	Ionic medium/ strength	$-\log K_{a_1}$	$-\log K_{a_2}$	Reference
20	0.1 M KNO_3	2.60	12.0	188
20	0.1 M KNO_3	2.60	12.0	84
25	0.1 M $NaClO_4$	2.49	11.74	12
25	0.1 M KNO_3	2.22 ± 0.02	11.40 ± 0.02	150
25	0.1 M KNO_3	2.67 ± 0.04	11.67 ± 0.03	120
25	0.1 M KNO_3	2.37 ± 0.02	11.49 ± 0.03	42
25	0.1 M KNO_3	2.50 ± 0.02	11.7 ± 0.05	102
25	0.1 M KNO_3	2.62		97
25	0.1	2.51 ± 0.01	11.72 ± 0.04	172
30	0.1 M KNO_3	2.68 ± 0.06	11.42 ± 0.03	166
20	0.1-0.15	2.62	11.95	138
25	0.5 M $NaClO_4$	2.33	11.46	20
25	0.5 M $NaClO_4$	2.30	11.41	111
25	0.5 M $NaNO_3$	2.39 ± 0.02	11.59 ± 0.03	122
25	0.5 M $NaClO_4$		11.47	118
25	1 M $NaClO_4$	2.30	11.47	115
25	1 M KNO_3	2.33 ± 0.02	11.32 ± 0.02	150
25	1 M KNO_3	2.30 ± 0.01		160
25	3 M $NaClO_4$	2.329 ± 0.004	11.389 ± 0.012	135
25	3 M $NaClO_4$		11.74 ± 0.05	4

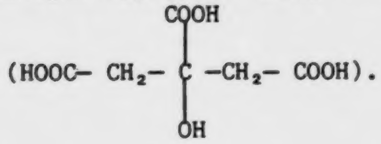
		$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	
20	0.1 M KNO_3	12.3	22.0	27.8	84

Table II-15. 1,2-Dihydroxybenzene (catechol) ().

Temp. (°C)	Ionic medium/ strength	$-\log K_{a_1}$	$-\log K_{a_2}$	Reference
20	0.1 M $NaClO_4$	9.45	12.8	6
20	0.1 M KNO_3	9.37	13.7	84
25(?)	0.1 M $NaClO_4$	9.4	13.4	169
25	0.1 M KNO_3	9.195 ± 0.002	12.98 ± 0.01	88
25	0.1 M KNO_3	9.26 ± 0.03	11.66 ± 0.05	42
25	0.1 M KNO_3	9.20 ± 0.01	11.93 ± 0.01	102
25	0.1 M KCl	9.21	11.70	7
25	0.1	9.32 ± 0.03	13.00	85
30	0.1 M KNO_3	9.13	11.59	123
25	0.1 M KNO_3	9.19		97
20	0.1-0.15	9.43	13.0	138
25	0.2 M $NaClO_4$	9.22	11.72	133
25	0.0	9.45	12.8	178
25	0.0	9.45	12.8	174
25	0.0	9.357		88

		$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	
20	0.1 M KNO_3	16.9	30.5	39.4	84

Table II-16. 2-Hydroxypropane-1,2,3-tricarboxylic acid (citric acid)



$$(HOOC-CH_2-\overset{\displaystyle COOH}{\underset{\displaystyle OH}{C}}-CH_2-COOH).$$

Temp. (°C)	Ionic medium/ strength	$-\log K_{a_1}$	$-\log K_{a_2}$	$-\log K_{a_3}$	Reference
20	0.1 M $NaClO_4$	2.96 ± 0.03	4.38 ± 0.02	5.68 ± 0.02	176
20	0.1 M $NaClO_4$	2.87	4.35	5.68	32
20	0.1 M KCl	2.95	4.40	5.76	129
25	0.1 M $NaClO_4$	2.93	4.37	5.64	156
25	0.1 M KNO_3	2.81 ± 0.08	4.36 ± 0.02	5.70 ± 0.02	58
25	0.1 M KNO_3	2.92	4.39	5.72	29
25	0.1 M KNO_3	2.85 ± 0.08	4.36 ± 0.02	5.70 ± 0.02	57
25	0.1 M KNO_3	2.79	4.30	5.65	151
25	0.1 M KNO_3	2.91	4.36	5.74	83
25	0.1 M KCl	2.892 ± 0.013	4.375 ± 0.013	5.685 ± 0.017	90
25	0.1	2.93	4.31	5.61	167
25	0.1	2.88	4.36	5.84	170
25	0.1	2.85	4.35	5.82	72
30	0.1 M $NaNO_3$	2.94	4.44	5.82	184
25	0.133	2.85	4.32		55
25	0.15	2.94	4.34	5.62	103
25	0.16 M NaCl	2.94	4.31	5.61	117
25	0.5	2.74	4.10	5.26	63
20	1 M NaCl	2.86 ± 0.07			13
25	1 M KNO_3	2.63	4.11	5.34	151
25	0.0	3.13	4.76	6.40	39
25	0.0	3.12	4.76	6.05	134
25	0.0	3.128 ± 0.0018	4.761	6.396 ± 0.0011	14
25	0.0	3.08	4.28	5.32	66
25	0.0	3.057	4.759	6.400	21
25	2 M $NaClO_4$	2.90 ± 0.07	4.16 ± 0.05	5.18 ± 0.03	26
		$\log \beta_1$	$\log \beta_2$		
20	0.1	7.37 ± 0.24	13.90 ± 0.48		196

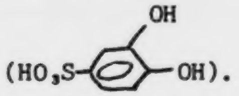
Table II-17. 4-Hydroxybenzoic acid (HO COOH).

Temp. (°C)	Ionic medium/ strength	$-\log K_{a_1}$	$-\log K_{a_2}$	Reference
20	0.1 M KNO_3	4.36	8.925	123
25	0.0	4.57	9.46	194
25	0.0	4.59		43
25	0.0	4.50		22
25	0.0	4.58		195
25	0.0	4.582		39
		$\log \beta_1$		
20	0.1	1.66 ± 0.13		196

Table II-18. 1-Hydroxyethane-1,3-dicarboxylic acid (malic acid) (HOOC-CH_2-CHOH-COOH).

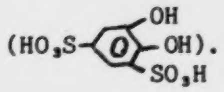
Temp. (°C)	Ionic medium/ strength	-log K_{a_1}	-log K_{a_2}	Reference
20	0.1 M $NaClO_4$	3.28 ± 0.02	4.72 ± 0.02	176
20	0.1 M $NaClO_4$	3.22	4.71	192
25	1 M $NaClO_4$	3.11 ± 0.04	4.46 ± 0.05	193
25	1 M KNO_3	2.77	4.44	190
25(?)	0.2	3.26	4.68	34
25	0.0	3.459	5.097	191
25	0.0	3.459	5.097	39
		log β_1	log β_2	
20	0.1	5.14 ± 0.03	8.52 ± 0.13	196

Table II-19. 1-2-Dihydroxybenzene-4-sulfonic acid (catechol-5-sulfonic acid)



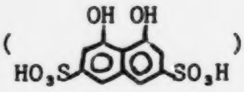
Temp. (°C)	Ionic medium/ strength	$-\log K_{a_1}$		$-\log K_{a_2}$	Reference
20	0.1 M $NaClO_4$	8.50		12.8	197
20	0.1 M KNO_3	8.50		12.8	84
30	0.1 M KNO_3	8.26		12.16	123
		$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	
20	0.1 M KNO_3	16.6	29.9	39.2	84

Table II-20. 1,2-Dihydroxybenzene-3,5-disulfonic acid (Tiron)



Temp. (°C)	Ionic medium/ strength	$-\log K_{a_1}$		$-\log K_{a_2}$	Reference
20	0.1 M $NaClO_4$	7.68		12.6	6
20	0.1 M KNO_3	7.66		12.6	188
20	0.1 M KNO_3	7.66		12.6	84
20	0.1 M KNO_3	7.66		12.6	205
20	0.1 M KCl	7.66 ± 0.02		12.6 ± 0.2	198
25	0.1 M $NaClO_4$	7.66 ± 0.02		12.55 ± 0.09	203
25(?)	0.1 M $NaClO_4$	7.66		12.6	169
25	0.1 M KNO_3	7.2			199
25	0.1 M KNO_3	7.67 ± 0.02		12.51 ± 0.04	200
25	0.1 M KNO_3	7.60 ± 0.04		12.60 ± 0.06	120
25	0.1 M KNO_3	7.57 ± 0.01		12.48	102
25	0.1 M KNO_3	7.61			97
25	0.1 M KNO_3	7.59 ± 0.01		12.48	42
25	0.1 M KCl	7.64		12.2	210
25	0.5 M $NaClO_4$	7.31		11.69	204
25	0.5 M $NaNO_3$	7.29 ± 0.04		11.85 ± 0.05	201
25	0.5 M KNO_3	7.39 ± 0.03		12.10 ± 0.11	200
25	1 M $NaClO_4$	7.25		11.83	202
25	1 M KNO_3	7.17		11.77 ± 0.03	200
25	0.0	7.9		12.9	200
30	0.1 M KNO_3	7.54		12.26	123
		$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	
20	0.1 M KNO_3	16.7	30.3	40.0	84
25	0.1	16.6	30.0		124
25	1.0	14.9	28.4		124
25	2.0	14.6	28.1		124
25	0.0	19.06	31.1	33.5	124

Table II-21. 1,8-Dihydroxynaphthalene-3,6-disulfonic acid (chromotropic acid)

().

Temp. (°C)	Ionic medium/ strength	$-\log K_{a_3}$	$-\log K_{a_4}$	Reference
20	0.1 M $NaClO_4$	5.44 ± 0.03		206
20	0.1 M KNO_3	5.33	15.6	84
20	0.1 M KNO_3	5.41	15.6	205
20	0.1 M KCl	5.45 ± 0.03	15.5 ± 0.1	209
20	0.1 M KCl	0.61 ± 0.02$^{\alpha}$	0.73 ± 0.03$^{\beta}$	209
25	0.1 M $NaClO_4$	5.5 ± 0.05	15.5	208
25	0.1 M KNO_3	5.38 ± 0.01	15.6	102
25	0.1 M KNO_3	5.32		97
25	0.1 M KNO_3	5.34 ± 0.01	15.6	42
25	0.1 M KNO_3	5.30 ± 0.1		207
25	0.5 M $NaClO_4$	5.13		204
		$\log \beta_1$	$\log \beta_2$	
20	0.1 M KNO_3	17.1	29.8	84

$^{\alpha}$ $-\log K_{a_1}$.

$^{\beta}$ $-\log K_{a_2}$.

References for Appendix II.0

1. Adell, B. 1939. Ueber die elektrolytische Dissoziation von Diacarbonsaeuren in Wasser und in waesserigen Alkalichloridloesungen. Z. Phys. Chem. A185: 161-206.

2. Agren, A. 1954. The complex formation between iron(III) ion and sulfosalicylic acid. Acta Chem. Scand. 8: 266-279.

3. Agren, A. 1954. The complex formation between iron(III) ion and some phenols. II. Salicylic acid and p-amino salicylic acid. Acta Chem. Scand. 8: 1059-1072.

4. Agren, A. 1955. The complex formation between iron(III) ion and some phenols. IV. The acidity constant of the phenolic group. Acta Chem. Scand. 9: 49-56.

5. Ahrland, S. 1951. On the complex chemistry of the uranyl ion. IV. The complexity of uranyl acetate. Acta Chem. Scand. 5: 199-219.

6. Anderegg, G. and Malik, S. 1970. Die Komplexbildungstendenz des dreiwertigen Antimons in waesseriger Loesung. Helv. Chim. Acta 53: 577-600.

7. Antikainen, P.J. and Witikainen, U. 1973. A comparative study on the ionization of catechol anions in aqueous solutions. Acta Chem. Scand. 27: 2075-2082.

8. Aplincourt, M., Noizet, D. and Hugel, R. 1972. Coordination du soufre en solution aqueuse: complexes du nickel(II) avec des amides des séries oxy et thio carboxyliques. Bull. Soc. Chim. Fr. 1972: 26-33.

9. Avedikian, L. 1966. Etude calorimétrique des reactions d'ionisation. Application de la méthode de dosage calorimétrique à la mesure des enthalpies de neutralisation et d'ionisation de quelques acides aliphatiques halogénés en solution aqueuse. Bull. Soc. Chim. Fr. 1966: 2570-2576.

10. Avedikian, L. and Dollet, N. 1967. Etude calorimétrique des reactions d'ionisation. III. Grandeurs thermodynamiques d'ionisation de l'eau et des acides acétique et benzoique dans les melanges eau-éthanol. Bull. Soc. Chim. Fr. 1967: 4551-4554.

11. Ballash, N.M., Robertson, E.B. and Sokolowski, M.D. 1970. Ionization of some weak acids in dimethyl sulphoxide and water mixtures. Trans. Faraday Soc. 66: 2622-2628.

12. Banks, C.V. and Sing, R.S. 1959. Composition and stability of 5-sulfosalicylate complexes of beryllium and copper. J. Am. Chem. Soc. 81: 6159-6163.

13. Barnes, J.C. and Briston, P.A. 1970. Lanthanum citrate complexes in acid solutions. J. Less-common Metals 22: 463-465.

14. Bates, R.G. and Pinching, G.D. 1949. Resolution of the dissociation constants of citric acid at 0° to 50°, and determination of certain related thermodynamic functions. J. Am. Chem. Soc. 71: 1274-1283.

15. Bates, R.G. 1951. Determination of dissociation constants in a mixture of two weak acids by electromotive force measurements. J. Am. Chem. Soc. 73: 2259-2261.

16. Bates, R.G. and Canham, R.G. 1951. Resolution of the dissociation constants of d-tartaric acid from 0° to 50°C. J. Res. Natl. Bur. Stand. 47: 343-348.

17. Bauer, R.F. and Smith, W.M. 1965. The mono-oxalato complexes of iron(III). Part I. Equilibria. Can. J. Chem. 43: 2755-2762.

18. Bell, R.P. and Waind, G.M. 1951. Reaction-kinetic investigation of the incomplete dissociation of salts. Part III. The decomposition of nitramide in solutions of some metal salts of carboxylic acids. J. Chem. Soc. 1951: 2357-2362.

19. Bell, R.P. and Miller, W.B.T. 1963. Dissociation constants of formic acid and formic acid-d. Trans. Faraday Soc. 59: 1147-1148.

20. Bertin, F. and Thomas, G. 1972. Contribution à l'étude des complexes du beryllium. III. Chelates polynucléaires hydroxylés avec le sulfo-5 salicylaldéhyde. Bull. Soc. Chim. Fr. 1972: 1665-1678.

21. Bjerrum, N. and Unmack, A. 1929. Elektrolytische Messungen mit Wasserstoffelektroden in Mischungen von Saeuren und Basen mit Salzen. Die Dissoziationskonstanten von Wasser, Phosphorsaeure, Citronensaeure und Glycin. Kgl. Danske Videnskabernes Selskab, Math.-Fys. Medd. 9: 1-208.

22. Bolton, P.D., Fleming, K.A. and Hall, F.M. 1972. A linear free energy-enthalpy-entropy relationship for ionization of benzoic acids. J. Am. Chem. Soc. 94: 1033-1034.

23. Bottari, E. and Ciavatta, L. 1965. Studio potenziometrico dei complessi Fe(II)-ossalato. Gazz. Chim. Ital. 95: 908-920.

24. Bottari, E. and Ciavatta, L. 1968. Studio potenziometrico dei complessi Al(III)-ossalato. Gazz. Chim. Ital. 98: 1004-1013.

25. Bottari, E. and Rufolo, A. 1968. Komplexe zwischen Eisen(II) und Tartrat-Ion. Monat. Chem. 99: 2383-2389.

26. Bottari, E. and Vicedomini, M. 1973. On the protonation of citrate ions in 2 M $NaClO_4$. J. Inorg. Nucl. Chem. 35: 1657-1663.

27. Braibanti, A., Loporati, E. and Dallavalle, F. 1970. The protonation constant of oxamic acid in aqueous solution and in water-tetrahydrofuran mixture, at different temperatures and ionic strengths. Inorg. Chim. Acta 4: 529-532.

28. Briggs, T.N. and Stuehr, J.E. 1974. Simultaneous determination of precise equivalence points and pK values from potentiometric data: single pK systems. Anal. Chem. 46: 1517-1521.

29. Briggs, T.N. and Stuehr, J.E. 1975. Simultaneous potentiometric determination of precise equivalence points and pK values of two- and three-pK systems. Anal. Chem. 47: 1916-1920.

30. Brockman, F.G. and Kilpatrick, M. 1934. The thermodynamic dissociation constant of benzoic acid from conductance measurements. J. Am. Chem. Soc. 56: 1483-1486.

31. Bunting, J.W. and Thong, K.M. 1970. Stability constants for some 1:1 metal-carboxylate complexes. Can. J. Chem. 48: 1654-1656.

32. Campi, E., Ostacoli, G., Meirone, M. and Saini, G. 1964. Stability of the complexes of tricarboxylic and citric acids with bivalent metal ions in aqueous solution. J. Inorg. Nucl. Chem. 26: 553-564.

33. Canady, W.J., Papee, H.M. and Laidler, K.J. 1958. Microcalorimetric studies of heats of neutralization and ionization of some weak acids in highly dilute aqueous solutions. Trans. Faraday Soc. 54: 502-506.

34. Cannan, R.K. and Kibrick, A. 1938. Complex formation between carboxylic acids and divalent metal cations. J. Am. Chem. Soc. 60: 2314-2320.

35. Cassol, A., DiBernardo, P., Portanova, R. and Magon, L. 1973. Interaction of MO_2^{2+} ions (M=U, Np, and Pu) with dicarboxylate ligands containing other donor atoms. Inorg. Chim. Acta 7: 353-358.

36. Chiacchierini, E. and Bartusek, M. 1969. Complexes of maltol with uranyl and aluminum. Coll. Czech. Chem. Commun. 34: 530-536.

37. Ciavatta, L., Nunziata, G. and Sillén, L.G. 1969. Iron(III) acetate complexes in aqueous 3 M $(Na^+)ClO_4^-$ medium. Acta Chem. Scand. 23: 1637-1652.

38. Choppin, G.R. and Schneider, J.K. 1970. The acetate complexing by trivalent actinide ions. J. Inorg. Nucl. Chem. 32: 3283-3288.

39. Christensen, J.J., Izatt, R.M. and Hansen, L.D. 1967. Thermodynamics of proton ionization in dilute aqueous solution. VII. $\Delta H°$ and $\Delta S°$ values for proton ionization from carboxylic acids at 25°. J. Am. Chem. Soc. 89: 213-222.

40. Christensen, J.J., Slade, M.D., Smith, D.E., Izatt, R.M. and Tsang, J. 1970. Thermodynamics of proton ionization in dilute aqueous solution. XIII. $\Delta G°$ (pK), $\Delta H°$, and $\Delta S°$ values for proton ionization from several methyl- and ethyl-substituted aliphatic carboxylic acids at 10, 25 and 40°. J. Am. Chem. Soc. 92: 4164-4167.

41. Coates, E. and Rigg, B. 1962. Complex formation Solochrome Violet R. Part 4. Some metal-dye stability constants. Trans. Faraday Soc. 58: 2058-2065.

42. Condike, G.F. and Martell, A.E. 1969. Mixed ligand chelates of copper (II). J. Inorg. Nucl. Chem. 31: 2455-2466.

43. Cottrell, T.L., Drake, G.W., Levi, D.L., Tully, K.J. and Wolfenden, J.H. 1948. The thermochemistry of solutions. Part V. The heats of ionization of some organic acids. J. Chem. Soc. 1948: 1016-1019.

44. DeBruin, H.J., Kairaitis, D. and Temple, R.B. 1962. The extraction of anionic beryllium complexes by tri-iso-octylamine. Aust. J. Chem. 15: 457-466.

45. Dellien, I., Grenthe, I. and Hessler, G. 1973. Thermodynamic properties of rare earth complexes. XVIII. Free energy, enthalpy, and entropy changes for the formation of some lanthanoid thiodiacetate and hydrogen thiodiacetate complexes. Acta Chem. Scand. 27: 2431-2440.

46. Deneux, M., Meilleur, R. and Benoit, R.L. 1968. Chélats du fer (III) avec des anions carboxilates. Can. J. Chem. 46: 1383-1388.

47. Dippy, J.F.J. and Williams, F.R. 1934. Chemical constitution and the dissociation constants of monocarboxylic acids. Part II. J. Chem. Soc. 1934: 1888-1892.

48. Dudeney, A.W.L. and Irving, R.J. 1975. Spectrophotometric investigations of aqueous solutions at elevated temperatures. J. Chem. Soc. Faraday Trans. 71: 1215-1220.

49. Dunsmore, H.S. and Speakman, J.C. 1954. Dissociation constant in mixed solvents. Part 1. Benzoic acid in dioxan + water. Trans. Faraday Soc. 50: 236-249.

50. Dunsmore, H.J. and Midgley, D. 1972. Thermodynamics of (+)-tartaric acid and its sodium and potassium complexes. J. Chem. Soc. Dalton 1972: 64-69.

51. Ernst, Z.L. and Menashi, J. 1962. The spectrophotometric determination of the dissociation constants of some substituted salicylic acids. Trans. Faraday Soc. 59: 230-240.

52. Ernst, Z.L., Irving, R.J. and Menashi, J. 1964. Calorimetric determination of the heats of the first and second ionization stages of salicylic acid. Trans. Faraday Soc. 60: 56-61.

53. Everett, D.H. and Wynne-Jones, W.F.K. 1939. The thermodynamics of acid-base equilibria. Trans. Faraday Soc. 35: 1380-1401.

54. Everett, D.H., Landsman, D.A. and Pinsent, B.R.W. 1952. The thermodynamics of ionization of some fatty acids. Proc. R. Soc. London A215: 403-415.

55. Feldman, I., North, C.A. and Hunter, H.B. 1960. Equilibrium constants for the formation of polynuclear tridentate 1:1 chelates in uranyl-malate, -citrate and -tartrate systems. J. Phys. Chem. 64: 1224-1230.

56. Fernandez, L.P. and Hepler, L.G. 1959. Thermodynamics of aqueous benzoic acid and the entropy of aqueous benzoate ion. J. Phys. Chem. 63: 110-112.

57. Field, T.B., McCourt, J.L. and McBryde, W.A.E. 1974. Composition and stability of iron and copper citrate complexes in aqueous solution. Can. J. Chem. 52: 3119-3124.

58. Field, T.B., Coburn, J., McCourt, J.L. and McBryde, W.A.E. 1975. Composition and stability of some metal citrate and diglycolate complexes in aqueous solution. Anal. Chim. Acta 74: 101-106.

59. Filipovic, I., Piljac, I., Bach-Dragutinovic, B., Kruhak, I. and Grabaric, B. 1973. Stability constants of zinc complexes with 3-hydroxypropionate and 2-, 3-, and 4-hydroxybutyrates. Croat. Chem. Acta 45: 447-452.

60. Fiordiponti, P., Rallo, F. and Rodante, F. 1974. The dissociation of benzoic acid in water-dimethylsulphoxide mixtures. Gazz. Chim. Ital. 104: 649-654.

61. Forrest, W.W. and Sturtevant, J.M. 1960. The heat of denaturation of ferrihemoglobin in acid solution. J. Am. Chem. Soc. 82: 585-589.

62. Friedman, S. and Pizer, R. 1975. Mechanism of the complexation of phenylboronic acid with oxalic acid. A reaction which requires ligand donor atom protonation. J. Am. Chem. Soc. 97: 6059-6062.

63. Furlani, C. and Cervone, E. 1962. Costanti di stabilità dei complessi zinco-citrato, zinco-tartrato, cadmio citrato e cadmio tartrato. Ann. Chim. (Rome) 52: 564-572.

64. Gerding, P. 1967. Thermochemical studies on metal complexes. IV. Free energy, enthalpy, and entropy changes of proton acetate complexes in aqueous solution. Acta Chem. Scand. 21: 2007-2014.

65. Gobom, S. 1974. The complex formation between tin(II) and acetate ion. Acta Chem. Scand. A28: 1180.

66. Gordienko, V.I. and Khudyakova, L.P. 1973. Concentrational dissociation constants of tartaric and citric acids at high ionic strengths. J. Gen. Chem. U.S.S.R. 43: 323-326.

67. Grenthe, I. and Tobiasson, I. 1963. Thermodynamic properties of rare earth complexes. I. Stability constants for the rare earth diglycolate complexes. Acta Chem. Scand. 17: 2101-2112.

68. Grenthe, I., Gardhammar, G. and Rundcrantz, E. 1969. Thermodynamic properties of rare earth complexes. VI. Stability constants for the oxalate complexes of Ce(III), Eu(III), Tb(III) and Lu(III). Acta Chem. Scand. 23: 93-108.

69. Grenthe, I. and Hansson, E. 1969. Thermodynamic properties of rare earth complexes. VII. Free energy, enthalpy, and entropy changes for the formation of scandium(III) diglycolate, dipicolinate, and malonate complexes at 25.00°C. Acta Chem. Scand. 23: 611-627.

70. Grenthe, I. and Ots, H. 1972. Thermodynamic properties of rare earth complexes. XI. Stability constants and free energy changes for the formation of rare earth diglycolate complexes at 5, 20, 35, and 50°C. Acta Chem. Scand. 26: 1217-1228.

71. Guilleme, J. and Wojtkowiak, B. 1969. Etude thermodynamique de la dissociation ionique des acids carboxyliques α-acétyléniques. Bull. Soc. Chim. Fr. 1969: 3007-3016.

72. Grzybowski, A.K., Tate, S.S. and Datta, S.P. 1970. Magnesium and manganese complexes of citric and isocitric acids. J. Chem. Soc. A: 214-245.

73. Haladjian, J., Sabbah, R. and Bianco, P. 1969. Contribution à l'étude de l'acide formique, des formiates de sodium et de potassium. III. Etude électrométrique de la neutralisation des solutions aqueuses d'acide formique par la soude ou la potasse, à 25°C, en milieux $NaClO_4$ = 5 M et KCl = 3 M. J. Chim. Phys. 66: 1824-1832.

74. Hamer, W.J. and Acree, S.F. 1945. Second dissociation constant of o-phthalic acid and related pH values of phthalate buffers from 0° to 60°C. J. Res. Natl. Bur. Stand. 35: 381-416.

75. Hamer, W.J., Pinching, G.D. and Acree, S.F. 1945. First dissociation constant of o-phthalic acid and related pH values of phthalate buffers from 0° to 60°C. J. Res. Natl. Bur. Stand. 35: 539-564.

76. Harned, H.S. and Ehlers, R.W. 1933. The dissociation constant of acetic acid from 0 to 60° centigrade. J. Am. Chem. Soc. 55: 652-656.

77. Harned, H.S. and Ehlers, R.W. 1933. The dissociation constant of propionic acid from 0 to 60°. J. Am. Chem. Soc. 55: 2379-2383.

78. Harned, H.S. and Embree, N.D. 1934. The ionization constant of formic acid from 0 to 60°. J. Am. Chem. Soc. 56: 1042-1044.

79. Harned, H.S. and Sutherland, R.O. 1934. The ionization constant of n-butyric acid from 0 to 60°. J. Am. Chem. Soc. 56: 2039-2041.

80. Harned, H.S. and Hickey, F.C. 1937. The ionization of acetic acid in aqueous sodium chloride solutions from 0 to 40°. J. Am. Chem. Soc. 59: 1284-1288.

81. Harned, H.S. and Hickey, F.C. 1937. Salt action on the ionization of acetic acid and hydrolysis of the acetate ion. J. Am. Chem. Soc. 59: 2303-2304.

82. Harned, H.S. and Fallon, L.D. 1939. The second ionization constant of oxalic acid from 0 to 50°. J. Am. Chem. Soc. 61: 3111-3113.

83. Harris, W.R. and Martell, A.E. 1976. Aqueous complexes of gallium (III). Inorg. Chem. 15: 713-720.

84. Havelkova, L. and Bartusek, M. 1969. Potentiometric investigation of the complexes of aluminum with o-diphenols, chromotropic acid and o-phenol carboxylic acids. Coll. Czech. Chem. Commun. 34: 3722-3731.

85. Huber, P.R., Griesser, R., Priss, B. and Sigel, H. 1969. Ternary complexes in solution. The stability increasing effect of the imidazole group on the formation of mixed Cu^{2+} complexes. Eur. J. Biochem. 10: 238-242.

86. Ivakin, A.A. and Voronova, E.M. 1973. Spectrophotometric study of formato-complexes of vanadium (IV). Russ. J. Inorg. Chem. 18: 817-820.

87. Izatt, R.M., Fernelius, W.C., Haas, C.G., Jr. and Block, B.P. 1955. Studies on coordination compounds. XI. Formation constants of some tervalent ions and the thorium (IV) ion with the acetylacetonate ion. J. Phys. Chem. 59: 170-174.

88. Jameson, R.F. and Wilson, M.F. 1972. Thermodynamics of the interactions of catechol with transition metals. Part I. Free energy, enthalpy, and entropy changes for the ionisation of catechol at 25°C. Comparison of the temperature-coefficient method with direct calorimetry. J. Chem. Soc. Dalton 1972: 2610-2614.

89. Jones, A.V. and Parton, H.N. 1952. The thermodynamic dissociation constant of benzoic acid and the entropy of the benzoate ion. Trans. Faraday Soc. 48: 8-11.

90. Kankare, J.J. 1972. Determination of dissociation constants of acids and bases by potentiostatic titrations. Anal. Chem. 44: 2376-2379.

91. Kereichuk, A.S. and Il'icheva, L.M. 1975. The formation of aluminum complexes of monocarboxylic acids. Russ. J. Inorg. Chem. 20: 1291-1293.

92. Kilpatrick, M. 1953. The dissociation constants of acids in salt solutions. I. Benzoic acid. J. Am. Chem. Soc. 75: 584-585.

93. Kilpatrick, M. and Eanes, R.D. 1953. The dissociation constants of acids in salt solutions. II. Acetic acid. J. Am. Chem. Soc. 75: 586-587.

94. Kilpatrick, M. and Eanes, R.D. 1953. The dissociation constants of acids in salt solutions. III. Glycolic acid. J. Am. Chem. Soc. 75: 587.

95. King, E.J. and Prue, J.E. 1961. Precise measurements, with the glass electrode, of the ionization constants of benzoic, phenylacetic, and β-phenylopropionic acids at 25°. J. Chem. Soc. 1961: 275-279.

96. Kolat, R.S. and Powell, J.E. 1962. Acetate complexes of the rare earth and several transition metal ions. Inorg. Chem. 1: 293-296.

97. Kugler, G.C. and Carey, G.M. 1970. Thermometric titration studies of mixed ligand complexes of thorium. Talanta 17: 907-914.

98. Larsson, E. and Adell, B. 1931. Die elektrolytische Dissoziation von Saeuren in Salzloesungen. I. Die Dissoziations-konstante der Essigsaeure und die Aktivitaetsverhaeltnisse ihrer Ionen in den Loesungen einiger Alkali-und Erdalkalichloride. Z. Phys. Chem. A156: 352-380.

99. Larsson, E. and Adell, B. 1931. Die elektrolytische Dissoziation von Saeuren in Salzloesungen. II. Die Dissoziationskonstanten einiger Fettsaeuren und die Aktivitaetsverhaeltnisse ihrer Ionen in Natriumchlorid und Kaliumchloridloesungen. Z. Phys. Chem. A156: 381-396.

100. Larsson, E. and Adell, B. 1931. Die elektrolytische Dissoziation von Saeuren in Salzloesungen. III. Die Dissoziationskonstanten einiger Saeuren und die Aktivitaetsverhaeltnisse ihrer Ionen in Natriumchlorid- und Kaliumchloridloesungen. Z. Phys. Chem. A157: 342-362.

101. Lee, Y.H. 1973. The association of 3-bromo-5-sulfosalicylic acid in aqueous solution. Acta Chem. Scand. 27: 1807-1815.

102. L'Heureux, G.A. and Martell, A.E. 1966. Mixed ligand chelates of copper (II). J. Inorg. Nucl. Chem. 28: 481-491.

103. Li, N.C., Lindenbaum, A. and White, J.M. 1959. Some metal complexes of citric and tricarballylic acids. J. Inorg. Nucl. Chem. 12: 122-128.

104. Libich, S. and Rabenstein, D.L. 1973. Nuclear magnetic resonance studies of the solution chemistry of metal complexes. Determination of formation constants of methylmercury complexes of selected carboxylic acids. Anal. Chem. 45: 118-124.

105. Lowe, B.M. and Smith, D.G. 1975. Dissociation constant of benzoic acid in H_2O-D_2O mixtures. J. Chem. Soc. Faraday Trans. 1(71): 389-397.

106. Lumme, P. and Kari, E. 1975. Phthalic acid as a reagent in inorganic qualitative analysis of metal ions. Part III. Thermodynamics of the protonation of phthalate ion in aqueous sodium perchlorate solutions. Acta Chem. Scand. A29: 117-124.

107. MacInnes, D.A. and Shedlovsky, T. 1931. The ionization constant of acetic acid. J. Am. Chem. Soc. 53: 2419-2420.

108. MacInnes, D.A. and Shedlovsky, T. 1932. The determination of the ionization constant of acetic acid, at 25°, from conductance measurements. J. Am. Chem. Soc. 54: 1429-1438.

109. McAuley, A. and Nancollas, G.M. 1960. Complex formations in solutions of copper oxalate. Trans. Faraday Soc. 56: 1165-1171.

110. McAuley, A. and Nancollas, G.M. 1961. Thermodynamics of ion association. Part VII. Some transition-metal oxalates. J. Chem. Soc. 1961: 2215-2221.

111. McBryde, W.A.E., Rohr, J.L., Penciner, J.S. and Page, J.A. 1970. Stability constants of three iron(III) salicylates. Can. J. Chem. 48: 2574-2586.

112. Maftoon, M.Y. 1972. Dissociation constant of acetic acid in water-acetone mixtures. Coll. Czech. Chem. Commun. 37: 688-692.

113. Manning, P.G. and Ramamoorthy, S. 1972. Equilibrium studies of metal-ion complexes of interest to natural waters. III. Simple and mixed dl- and meso tartrate complexes of Al(III), In(III), and Pb(II). J. Inorg. Nucl. Chem. 34: 1997-2005.

114. Martin, D.L. and Rossotti, F.J.C. 1959. The hydrogen-bonding of monocarboxylates in aqueous solution. Proc. Chem. Soc. 1959: 60.

115. Martin, R.P. and Paris, R.A. 1964. Formation et stabilite d'un chelate mixte dans le systeme cuivre-glycine-acide sulfo-5 salicylique en solution aqueuse. Bull. Soc. Chim. Fr. 1964: 80-85.

116. Matsui, T., Ko, H.C. and Hepler, L.G. 1974. Calorimetric heats of ionization of aqueous benzoic acid from 5-100°C and derived thermodynamic quantities. Can. J. Chem. 52: 2912-2918.

117. Matsushima, Y. 1963. Determination of complex stability constants by ion exchange method. (Extension of Schubert's method to lower pH region.) Chem. Pharm. Bull. 11: 566-570.

118. Migal, P.K., Gerbeleu, A.P. and Muntyanu, G.G. 1975. Enthalpy and entropy of formation of mixed complexes in copper(II) ion-5-sulpho-salicylic acid-α-aminoacid systems. Russ. J. Inorg. Chem. 20: 1320-1322.

119. Miyazaki, M., Shimoishi, Y., Miyata, H. and Toei, K. 1974. The reaction of dicarboxylic acids containing ether linkages with alkaline earth metals. J. Inorg. Nucl. Chem. 36: 2033-2038.

120. Mont, G.E. and Martell, A.E. 1966. Equilibria involving the formation, hydrolysis, and olation of oxovanadium(IV) chelate in aqueous solution. J. Am. Chem. Soc. 88: 1387-1393.

121. Moorhead, E.G. and Sutin, N. 1966. Rate and equilibrium constants for the formation of the monooxalate complex of iron(III). Inorg. Chem. 5: 1866-1871.

122. Morin, M., Paris, M.R. and Scharff, J.P. 1971. Etude potentiométrique et spectrophotométrique de la complexation des ions ferriques par l'acide sulfo-5-salicylique. Anal. Chim. Acta 57: 123-129.

123. Murakami, Y., Nakumura, K. and Tokunaga, M. 1963. Stability order in metal chelate compounds. I. 4-carboxy- and 4-sulfocatechol complexes. Bull. Chem. Soc. Jpn. 36: 669-675.

124. Naesaenen, R. 1957. Studies on the stability of aluminum chelates of catecholdisulphuric acid in aqueous solutions. Acta Chem. Scand. 11: 1308-1312.

125. Nagata, K., Umayahara, A. and Tsuchiya, R. 1965. Formation constants of chromium(III)-oxalate complexes. Bull. Chem. Soc. Jpn. 38: 1059-1061.

126. Napoli, A. and Liberti, A. 1970. Studio potenziometrico dei complessi tra lo ione alluminio e gli acidi ftalico e benzoico. Gazz. Chim. Ital. 100: 906-915.

127. Napoli, A. 1972. Aluminum complexes with diglycolic and thiodiglycolic acids. J. Inorg. Nucl. Chem. 34: 1225-1231.

128. O'Hara, W.F. 1975. Thermodynamics of ionization of benzoic acid in water at 298°K. J. Solution Chem. 4: 793-796.

129. Okac, A. and Kolarik, Z. 1959. Potentiometrische Untersuchung der Zitratkomplexe des Zinks. Coll. Czech. Chem. Commun. 24: 1-8.

130. Okac, A. and Kolarik, Z. 1959. Potentiometrische Untersuchung von Komplexsalzen der Kojisaeure in waessrigen Loesungen. Coll. Czech. Chem. Commun. 24: 266-272.

131. Palmaeus, R. and Kierkegaard, P. 1964. Equilibrium studies on phthalate ions. On the association between o-phthalate ions and protons in 3 M (Na)ClO_4. Acta Chem. Scand. 18: 2226-2232.

132. Park, M.V. 1966. Complex formation between iron(II) and some substituted salicylic acids. J. Chem. Soc. A: 816-820.

133. Patel, D.C. and Bhattacharya, P.K. 1971. A study of ligand exchange in some nickel complexes. J. Inorg. Nucl. Chem. 33: 529-533.

134. Pearse, K.N. and Creamer, L.K. 1975. The complete ionization scheme for citric acid. Aust. J. Chem. 28: 2409-2415.

135. Pecsok, R.L. and Schaefer, W.P. 1961. Salicylate and 5-sulfosalicylate complexes of chromium(II). J. Am. Chem. Soc. 83: 62-65.

136. Pedersen, K.J. 1934. The decomposition of α-nitrocarboxylic acid. J. Phys. Chem. 38: 559-571.

137. Pedersen, K.J. 1949. The effect of metal ions on the rate of decomposition of nitroacetic acid. Acta Chem. Scand. 3: 676-696.

138. Perrin, D.D. 1958. Stability of metal complexes with salicylic acid and related substances. Nature (London) 182: 741-742.

139. Perrin, D.D. 1959. The stability of iron complexes. Part IV. Ferric complexes with aliphatic acids. J. Chem. Soc. 1959: 1710-1777.

140. Perrin, D.D., Sayce, I.G. and Sharma, V.S. 1967. Mixed ligand complex formation by copper(II) ion. J. Chem. Soc. A 1967: 1755-1759.

141. Persson, H. 1971. The complex formation in the zinc acetate and the proton acetate system. Acta Chem. Scand. 25: 1775-1789.

142. Pinching, G.D. and Bates, R.G. 1948. Second dissociation constant of oxalic acid from 0° to 50°C, and the pH of certain oxalate buffer solutions. J. Res. Natl. Bur. Stand. 40: 405-416.

143. Podlaha, J. and Podlahova, J. 1970. Metal complexes of thiopolycarboxylic acids. I. Complexes of thiodiacetic acid in solution. Inorg. Chim. Acta 4: 521-525.

144. Portanova, R., Tomat, G., Cassol, A. and Magnon, L. 1972. Equilibria of thorium(IV) with monocarboxylate ligands. J. Inorg. Nucl. Chem. 34: 1685-1690.

145. Powell, J.E., Kolat, R.S. and Paul, G.S. 1964. Stability constants of the rare earth chelate species formed with some monocarboxylate ligands. Inorg. Chem. 3: 518-520.

146. Prue, J.E. and Read, A.J. 1966. Acidity constant of formic acid. Trans. Faraday Soc. 62: 1271-1274.

147. Prue, J.E., Read, A.J. and Romeo, G. 1971. Specific interactions of tetra-alkylammonium and alkali metal cations with anions in aqueous solutions. Trans. Faraday Soc. 67: 420-427.

148. Purdie, N., Tomson, M.B. and Cook, G.K. 1972. Determination of composition of mixtures of diastereoisomeric forms of weak acids by pH titration. Anal. Chem. 44: 1521-1530.

149. Purdie, N. and Tomson, M.B. 1973. Thermodynamics of ionization of diastereoisomeric forms of 2,3-dicarboxylic acids. J. Am. Chem. Soc. 95: 48-50.

150. Rajan, K.S. and Martell, A.E. 1964. Equilibrium studies of uranyl complexes. I. Interaction of uranyl ion with some hydroxycarboxylic acids and amino-carboxylic acids. J. Inorg. Nucl. Chem. 26: 789-798.

151. Rajan, K.S. and Martell, A.E. 1965. Equilibrium studies of uranyl complexes. III. Interaction of uranyl ion with citric acid. Inorg. Chem. 4: 462-469.

152. Rajan, K.S. and Martell, A.E. 1967. Equilibrium studies of uranyl complexes. IV. Reactions with carboxylic acids. J. Inorg. Nucl. Chem. 29: 523-529.

153. Ramamoorthy, S., Raghavan, A. and Santappa, M. 1969. Complexes of uranyl ion with butyric and isobutyric acids. J. Inorg. Nucl. Chem. 31: 1765-1769.

154. Ramamoorthy, S. and Santappa, M. 1969. Stability constants of some uranyl complexes. II. Bull. Chem. Soc. Jpn. 42: 411-416.

155. Ramamoorthy, S. and Manning, P.G. 1972. Equilibrium studies of metal-ion complexes of interest to natural waters. I. Simple and mixed complexes of dl- and meso-tartaric acid with Fe(III), La(III) and Nd(III) ions. J. Inorg. Nucl. Chem. 34: 1977-1987.

156. Ramamoorthy, S. and Manning, P.G. 1973. Equilibrium studies of metal-ion complexes of interest to natural waters. VI. Simple and mixed complexes of Fe(III) involving NTA as primary ligand and a series of oxygen-bonding organic anions as secondary ligands. J. Inorg. Nucl. Chem. 35: 1571-1575.

157. Robinson, R.A. and Biggs, A.I. 1957. The ionization constants of p-aminobenzoic acid in aqueous solution at 25°C. Aust. J. Chem. 10: 128-134.

158. Rodante, F., Rallo, F. and Fiordiponti, P. 1974. Ionization enthalpy of benzoic acid in water-dimethylsulphoxide mixtures. Thermochim. Acta 9: 269-275.

159. Saarinen, H., Melnik, M. and Maekitie, O. 1969. The acid strength of propionic, 2-bromopropionic and 3-bromopropionic acids in aqueous potassium chloride solutions. Acta Chem. Scand. 23: 2542-2543.

160. Saini, G. and Mentasti, E. 1970. Kinetics and formation of the monosulfosalicylic complex of iron(III). Inorg. Chim. Acta 4: 210-214.

161. Saxton, B. and Darken, L.S. 1940. The ionization constant of weak acids at 25° from conductance measurements. A method of extrapolating the data. J. Am. Chem. Soc. 62: 846-852.

162. Saxton, B. and Langer, T.W. 1933. The ionization constants of monochloracetic acid, at 25°, from conductance measurements. J. Am. Chem. Soc. 55: 3638-3645.

163. Saxton, B. and Meier, H.F. 1934. The ionization constants of benzoic acid and of the three monochlorbenzoic acids, at 25°C, from conductance measurements. J. Am. Chem. Soc. 56: 1918-1921.

164. Sekine, T. 1965. Solvent extraction study of trivalent actinide and lanthanide complexes in aqueous solutions. III. Oxalate complexes of La(III), Eu(III), Lu(III), and Am(III) in 1 M $NaClO_4$. Acta Chem. Scand. 19: 1476-1482.

165. Simeon, V., Ivicic, N. and Tkalcec, M. 1972. Construction of a single reaction calorimeter and heats of some standard reactions at 20°C. Z. Phys. Chem. (Frankfurt) 78: 1-12.

166. Singth, S.P. and Tandon, J.P. 1975. pH-metric studies on the binary and ternary complexes of oxovanadium(IV). Monatsh. Chem. 106: 271-282.

167. Skorik, N.A. and Kumok, V.N. 1971. Protonation of the anions of certain acids in aqueous alcoholic solutions. Russ. J. Inorg. Chem. 16: 1643-1645.

168. Solladie-Cavallo, A. 1966. Détermination potentiométrique des constantes d'ionisation thermodynamiques de quelques diacides des séries oxydiacétique et thiodiacétique. C.R. Acad. Sci. Paris Sect. C 263: 93-95.

169. Sommer, L., Sepel, T. and Kurilova, L. 1965. Komplexe des Uranyls mit phenolischen Liganden. IV. Spektrophotometrische Untersuchung des Reaktion mit Tiron und Brenzcatechin. Coll. Czech. Chem. Commun. 30: 3834-3860.

170. Tate, S.S., Grzybowski, A.K. and Datta, J.P. 1965. The stability constants of magnesium citrate complexes. J. Chem. Soc. 1965: 3905-3912.

171. Tedesco, P.M. and Walton, H.F. 1969. Metal complexes of "squaric acid" (Diketocyclobutenediol) in aqueous solution. Inorg. Chem. 8: 932-937.

172. Thankur, N.V., Jogdeo, S.M. and Kanekar, C.R. 1966. Complex formation between gadolinium ions and 5-sulphosalicylic acid. J. Inorg. Nucl. Chem. 28: 2297-2305.

173. Tichane, R.M. and Bennett, W.E. 1957. Coordination compounds of metal ions with derivatives and analogs of aminodiacetic acid. J. Am. Chem. Soc. 79: 1293-1296.

174. Timberlake, C.F. 1957. A potentiometric and polarographic study of copper-catechol complexes. J. Chem. Soc. 1957: 4987-4993.

175. Timberlake, C.F. 1964. Iron-tartrate complexes. J. Chem. Soc. 1964: 1229-1240.

176. Timberlake, C.F. 1964. Iron-malate and iron-citrate complexes. J. Chem. Soc. 1964: 5078-5085.

177. Travers, J.G., McCurdy, K.G., Dolman, D. and Hepler, L.G. 1975. Glass-electrode measurements over a wide range of temperatures: The ionization constants (5-90°C) and thermodynamics of ionization of aqueous benzoic acid. J. Solution Chem. 4: 267-274.

178. Tyson, C.A. and Martell, A.E. 1968. Equilibria of metal ions with pyrocatechol and 3,5-di-t-butylpyrocatechol. J. Am. Chem. Soc. 90: 3379-3386.

179. Vasilev, V.P., Kochergina, L.A. and Eremenko, V.I. 1971. Heat of first dissociation of oxalic acid at 25°C in the presence of various electrolytes. Russ. J. Phys. Chem. 45: 1196-1197.

180. Vasilev, V.P., Shekhanova, L.P. and Kochergina, L.A. 1973. Heat of ionization of oxalic acid in presence of various electrolytes. J. Gen. Chem. U.S.S.R. 43: 967-970.

181. Votava, J. and Bartusek, M. 1975. Complexes of beryllium with five- and six-membered chelate rings. Coll. Czech. Chem. Commun. 40: 2050-2058.

182. Voznakova, Z. and Strafelda, F. 1971. Dissoziationskonstanten einiger Saeuren in Wasser-Methanol-Gemischen. Coll. Czech. Chem. Commun. 36: 2993-3003.

183. Wadsoe, I. 1962. Heats of hydrolysis of N-acetyl imidazole and butyl acetamide in aqueous solution. Acta Chem. Scand. 16: 479-486.

184. Warner, R.C. and Weber, I. 1953. The cupric and ferric citrate complexes. J. Am. Chem. Soc. 75: 5086-5094.

185. Wilson, J.M., Gore, N.E., Sawbridge, J.E. and Cardenas-Cruz, F. 1967. Acid-base equilibria of substituted benzoic acids. Part 1. J. Chem. Soc. B 1967: 852-859.

186. Yasuda, M., Suzuki, K. and Yamasaki, K. 1956. Stability of copper and nickel chelates of some phthalic acid derivatives. J. Phys. Chem. 60: 1649-1651.

187. Yasuda, M., Yamasaki, K. and Ohtaki, H. 1960. Stability of complexes of several carboxylic acids formed with bivalent metals. Bull. Chem. Soc. Jpn. 3: 1067-1070.

188. Zelinka, J. and Bartusek, M. 1971. Potentiometrische Untersuchung der Bildung von Komplexen des Vanadyls mit o-diphenolen und o-phenol-carbonsaeuren. Coll. Czech. Chem. Commun. 36: 2615-2624.

189. Ciavatta, L. and Villafiorita, M. 1965. Studio potenziometrico dei complessi Fe(II)-ossalato. Gazz. Chim. Ital. 95: 908-920.

190. Rajan, K.S. and Martell, A.E. 1964. Equilibrium studies of uranyl complexes. II. Interaction of uranyl ion with tartaric and malic acids. J. Inorg. Nucl. Chem. 26: 1927-1944.

191. Eden, M. and Bates, R.G. 1959. Resolution of the dissociation constants of d,l-malic acid from 0° to 50°C. J. Res. Natl. Bur. Stand. 62: 161-170.

192. Campi, E. 1963. Complessi di ioni metallici con gli acidi tartronico, malico, malonico e succinico. Ann. Chim. (Rome) 53: 96-116.

193. Bottari, E. and Liberti, A. 1968. Ossiacidi come agenti legandi. L'acido malico e i suoi complessi con Pb(II). Gazz. Chim. Ital. 98: 991-1003.

194. Sager, E.E., Schooley, M.R., Carr, A.S. and Acree, S.F. 1945. Ultraviolet spectra and dissociation constants of p-hydroxybenzoic acid, methyl, ethyl, n-butyl, and benzyl p-hydroxy benzoate and potassium p-phenolsulfonate. J. Res. Natl. Bur. Stand. 35: 521-538.

195. Briegler, G. and Bieber, A. 1951. Dissoziationskonstanten substituierter Benzoesaeure bei verschiedenen Temperaturen und thermodynamische Groessen der Saeuredissoziation. Z. Elektrochem. 55: 250-259.

196. Ng Kee Kwong, K.F. and Huang, P.M. 1979. The relative interference of low-molecular-weight, complexing organic acids on the hydrolysis and precipitation of aluminum. Soil Sci. 128: 337-342.

197. Bartusek, M. and Sommer, L. 1965. On the complex forming tendency of phenolic hydroxyl with UO_2^{2+}. J. Inorg. Nucl. Chem. 27: 2397-2412.

198. Schwarzenbach, G. and Willi, A. 1951. Metallindikatoren. III. Die Komplexbildung der Brenzcatechin-3,5-disulfosaeure (=Tiron) mit dem Eisen(III)-ion. Helv. Chim. Acta 34: 528-539.

199. Martell, A.E., Chaberek, S., Jr., Courtwey, R.C., Westerback, S. and Hyytiainen, H. 1957. Hydrolytic tendencies of metal chelate compounds. I. Cu(II) chelates. J. Am. Chem. Soc. 79: 3036-3041.

200. McBryde, W.A.E. 1964. A spectrophotometric reexamination of the spectra and stabilities of the iron(III)-tiron complexes. Can. J. Chem. 42: 1917-1927.

201. Morin, M. and Scharff, J.P. 1972. La chélation des ions fer(III) par l'acide pyrocatechol disulfonique-3,5. Anal. Chim. Acta 60: 101-108.

202. Scharff, J.P. and Genin, R. 1975. Chélates du manganese(II) avec des coordinats phénoliques. Partie I. Complexes simples binaires. Anal. Chim. Acta 78: 201-209.

203. Sigel, H., Huber, P.R., Griesser, R. and Prijs, B. 1973. Ternary complexes in solution. XV. Mixed-ligand copper(II) complexes with 2,2'-bipyridyl or 1,10-phenanthroline and pyrocatecholate or derivatives thereof. Inorg. Chem. 12: 1198-1200.

204. Lajunen, L.H.J. 1975. Formation of metal chelates with sulpho-substituted aromatic hydroxy carboxylic acids. Part III. Mixed ligand copper(II) chelates of 3,5-disulphosalicylic, 3-hydroxy-5,7-disulpho-2-naphthoic and catechol-3,5-disulphonic acids. Finn. Chem. Lett. 1975: 1-5.

205. Bartusek, M. and Zelinka, J. 1967. Potentiometrische Untersuchung der Berylliumkomplexe mit o-Diphenolen, 1,8-Dihydroxy-naphtalinderivaten und o-Phenolcarbonsaeuren. Coll. Czech. Chem. Commun. 32: 992-1005.

206. Sakaguchi, M., Mizote, A., Miyata, H. and Toei, K. 1963. Chromotropic acid and its zirconyl and thorium complexes. Bull. Chem. Soc. Jpn. 36: 885-888.

207. Wake, R., Miyata, H. and Toei, K. 1968. Investigation of copper (II) chelate with chromotropic acid. Bull. Chem. Soc. Jpn. 41: 1452-1453.

208. Bertoglio Riolo, C., Fulle Soldi, T., Gallotti, G. and Pesavento, M. 1974. Potentiometric determination of stability constants with ion-selective electrodes. Chelates between copper(II) and chromotropic acid and chromotrop-2B. Gazz. Chim. Ital. 104: 193-200.

209. Budnesinsky, B. 1969. Acidity of several chromotropic acid azo derivatives. Talanta 17: 1277-1288.

210. Naesaenen, R. 1959. Studies of some metal complexes of catechol-3,5-disulphonic acid. Acta Chem. Scand. 13: 869-876.

211. Baker, J.P. and Schofield, C.L. 1980. Aluminum toxicity to fish as related to acid precipitation and Adirondack surface water quality. Int. Conf. on Ecological Impact of Acid Precipitation, Sandefjord, Norway, March 11-14, 1980.

212. Driscoll, C.T., Baker, J.P., Bisogni, J.J. and Schofield, C.L. 1980. Effect of aluminum speciation in fish in dilute acidified waters. Nature (London) 284: 161-164.

213. Grahn, O. 1980. Fish kills due to high aluminum concentration in lake water. Int. Conf. on Ecological Impact of Acid Precipitation, Sandefjord, Norway, March 11-14, 1980.

214. Muniz, I.P. and Leivestad, H. 1980. Toxic effects of aluminium on the brown trout, *Salmo trutta*. Int. Conf. on Ecological Impact of Acid Precipitation, Sandefjord, Norway, March 11-14, 1980.

APPENDIX III.0

Freshwater Aluminum Studies

APPENDIX III.0

Freshwater Aluminum Studies

Table III-1. Listing of principal investigators who kindly provided some unpublished data included in Chapters 2 and 3.

Principal investigator	Topic	Address
Peter Campbell	Al speciation in surface water	INRS-Eau 2700 Einstein C.P. 7400 Ste-Foy, P.Q. C1V 4C7
Karen L. Clark	Al toxicity to tadpoles in Ontario	Biota Environmental Contractors P.O. Box 21 Dorset, Ontario POA 1E0
Irena Creed	Al content of zooplankton in soft-water lakes	Institute for Environmental Studies University of Toronto Toronto, Ontario M5S 1A4
Charles T. Driscoll	Al speciation in surface water	Department of Civil Engineering Syracuse University Syracuse, New York 13210
A. Dufresne	Al speciation in surface water	Department of Renewable Resources Macdonald College McGill University Ste-Anne de Bellevue, P.Q. H9Y 1C0
Ronald J. Hall	Al and stream invertebrates	Dorset Research Centre Ontario Ministry of the Environment P.O. Box 39 Dorset, Ontario POA 1E0

Table III-1. (Cont'd)

Principal investigator	Topic	Address
Harold Harvey	Al and fish mortality	Department of Zoology University of Toronto Toronto, Ontario M5S 1A4
Magda Havas	Al localization in aquatic plants and animals	Institute for Environmental Studies University of Toronto Toronto, Ontario M5S 1A4
William H. Hendershot	Al speciation in surface water	Department of Renewable Resources Macdonald College McGill University Ste-Anne de Bellevue, P.Q. H9Y 1C0
Thomas C. Hutchinson	Al-tolerant algae	Institute for Environmental Studies University of Toronto Toronto, Ontario M5S 1A4
Bruce D. LaZerte	Al speciation in surface water; Al toxicity to tadpoles	Dorset Research Centre Ontario Ministry of the Environment P.O. Box 39 Dorset, Ontario P0A 1E0
Tiina Pajos	Al content of aquatic macrophytes in soft-water lakes	Institute for Environmental Studies University of Toronto Toronto, Ontario M5S 1A4
Brian J. Paul	Al effects on ^{32}P-PO$_4$ and ^{14}C uptake by algae	Department of Botany University of Toronto Scarborough College Toronto, Ontario M5S 1A4

Table III-1. (Cont'd)

Principal investigator	Topic	Address
R. Playle	Al speciation and determination in water	Department of Geology McMaster University Hamilton, Ontario L8S 4L8
Debbie Roberts	Distribution of aquatic macrophytes in soft-water lakes, N.Y. and N.H.	Department of Biology and Freshwater Institute Rensselaer Polytechnic Institute Troy, New York 12181
Robert Singer	Distribution of aquatic macrophytes in soft-water lakes, N.Y. and N.H.	School for Field Studies 196 Broadway Cambridge, Massachusetts 02139
Pamela M. Stokes and Peter Turner	Al-tolerant and Al-sensitive strains of the alga, *Mougeotia*	Institute for Environmental Studies University of Toronto Toronto, Ontario M5S 1A4

APPENDIX IV.0

Abbreviations Used in the Text

APPENDIX IV.0

Abbreviations Used in the Text

a	year (annum)
AA	atomic absorption
ADP	adenosine diphosphate
AES	atomic emission spectroscopy
ALS	amyotrophic lateral sclerosis
ATPase	adenosine triphosphatase
CEC	cation-exchange capacity
CPE	conventional polyethylene
DC	direct current
DES	dialysis encephalopathy syndrome
DNA	deoxyribonucleic acid
DOC	dissolved organic carbon
EDTA	ethylenediaminetetraacetic acid
ELA	Experimental Lakes Area
eq	equivalents
ESCA	electron spectroscopy for chemical analysis
FAA	flameless atomic absorption
FEP	Teflon
GABA	gamma amino butyric acid
GC	gas chromatography
h	hour
ha	hectare
ICP	inductively coupled plasma
LPE	linear polyethylene
MW	molecular weight
PD	Parkinson-dementia
PTH	parathyroid hormone
RNA	ribonucleic acid
s	second
SD	standard deviation
SRM	standard reference material
TL_{50}	concentration of aluminum resulting in death of 50% of test fish within stated time
TLM	threshold level (mean)
TOC	total organic carbon
UV	ultraviolet

REFERENCES

Abbey, S. 1977. Studies in "standard sample" for use in the general analysis of silicate rocks and minerals. 5. 1977 edition of "usable" values. Geological Survey of Canada, Pap. 77-34.

Abrahamsen, G. 1983. Sulphur pollution: Ca, Mg, and Al in soil and soil water and possible effects on forest trees. In Effects of accumulation of air pollutants in forest ecosystems. Edited by B. Ulrich and J. Pankrath. D. Reidel Publ. Co., Boston. pp. 207-218.

Abrahamsen, G. and Stuanes, A.O. 1980. Effects of simulated acid rain on the effluent from lysimeters with acid, shallow soil rich in organic matter. In Proc. Int. Conf. Ecological Impact Acid Precipitation, Norway. Edited by D. Drablos and A. Tollan. SNSF Project. pp. 152-153.

Abruma, F., Pearson, R.W. and Elkins, C.B. 1958. Quantitative evaluation of soil reaction and base status changes resulting from field application of residually acid-forming nitrogen fertilizers. Soil Sci. Soc. Am. Proc. 22: 539-542.

Ackrill, P., Ralston, A.J., Day, J.P. and Hodge, K.C. 1980. Successful removal of aluminum from patient with dialysis encephalopathy. Lancet 2: 692-693.

Adams, F. and Lund, Z.F. 1966. Effect of chemical activity of soil solution aluminum on cotton root penetration of acid subsoils. Soil Sci. 101: 193-198.

Akitt, J.W. and Farthing, A. 1981. Hydrolysis of hexa-aqua-aluminum (III) in organic media. J. Chem. Soc. Dalton 1981: 1233-1234.

Akitt, J.W., Greenwood, N.N., Khandelual, B.L. and Lester, G.D. 1972. Al^{27} NMR studies of the hydrolysis and polymerisation of the hex-aquo Al(III) cation. J. Chem. Soc. Dalton Trans. 1972: 604-610.

Alderman, F.R. and Gitelman, H.J. 1980. Improved electrothermal determination of aluminum in serum by atomic absorption spectroscopy. Clin. Chem. 26(2): 258-260.

Alfrey, A.C., Le Gendre, G.R. and Kaehny, W.D. 1976. The dialysis encephalopathy syndrome. Possible aluminum intoxication. N. Engl. J. Med. 294: 184-188.

Alfrey, A.C., Hegg, A., Miller, N., Berl, T. and Berns, A. 1979. Interrelationship between calcium and aluminum metabolism in dialysed uremic patients. Mineral Electrolyte Metab. 2: 81-87.

Alfrey, A.C., Hegg, A. and Craswell, P. 1980. Metabolism and toxicity of aluminum in renal failure. Am. J. Clin. Nutr. 33: 1509-1516.

Allain, P. and Mauras, Y. 1979. Determination of aluminum in blood, urine and water by inductively coupled plasma emission spectrometry. Anal. Chem. 51(13): 2089-2091.

Almer, B., Dickson, W., Ekstrom, C., Hornstrom, E. and Miller, U. 1974. Effects of acidificaton on Swedish lakes. Ambio 3: 30-36.

Alpert, N.R. and Gordon, M.S. 1962. Myofibrillar adenosine triphosphatase activity in congestive heart failure. Am. J. Physiol. 202: 940-946.

Andelman, J.B. 1973. Incidence, variability and controlling factors for trace elements in natural, fresh waters. In Trace metals and metal organic interactions in natural waters. Edited by P.C. Singer. Ann Arbor Sci. Publ., Ann Arbor, Michigan. pp. 57-88.

Andersen, C.A. and Hinthorne, J.R. 1972. Ion microprobe mass analyses. Science 175: 853-860.

Anderson, B.G. 1948. The apparent thresholds of toxicity to Daphnia magna for chlorides of various metals when added to Lake Erie water. Trans. Am. Fish. Soc. 78: 96-113.

Aniol, A. 1983. Aluminum uptake by roots of two winter wheat varieties of different tolerance to aluminum. Biochem. Physiol. Pflanzen. 178: 11-20.

Anonymous. 1984. Landesantstalt für Immissionsschutz des Landes Nordrhein-Westfalen. Essen, Wallneyer Strasse 6.

Aoyagi, S., Haga, M., Aomori, M. and Yokozuka, N. 1972. Corrosion of aluminum by bacteria. II. Growth conditions of aluminum-corrosive bacteria and incorporation of aluminum into their cells. Pamagawa Daigaku Nogakubu Kenkyu Hokoku 12: 10. (Chem. Abstr. 81, 60662, 1974.)

Arieff, A.I., Cooper, J.D., Armstrong, D. and Lazarowitz, V.C. 1979. Dementia, renal failure and brain aluminum. Ann. Intern. Med. 90: 741-747.

Armiger, W.H., Foy, C.D., Fleming, A.L. and Caldwell, B.E. 1968. Differential tolerance of soybean varieties to an acid soil high in exchangeable aluminum. Agron. J. 60: 67-70.

Armson, K.A. 1977. Forest soils. Univ. of Toronto Press, Toronto, Ontario.

Asman, W.A.H. and Slanina, J. 1980. Meteorological interpretation of the chemical composition of precipitation and some results of sequential rain sampling. Proc. Int. Conf. Ecological Impact Acid Precipitation, Norway. Edited by D. Drablos and A. Tollan. SNSF Project. pp. 140-141.

Aveston, J. 1965. Hydrolysis of the aluminum ion: ultracentrifugation and acidity measurements. J. Chem. Soc. 1965: 4438-4443.

Awad, A.S., Edwards, D.G. and Milham, P.J. 1976. Effect of pH and phosphate on soluble aluminum and on growth and composition of kikuyu grass. Plant Soil 45: 531-542.

Bache, B.W. 1974. Soluble aluminum and calcium-aluminum exchange in relation to the pH of dilute calcium chloride suspensions of acid soils. J. Soil Sci. 25: 320-332.

Bache, B.W. and Crooke, W.M. 1981. Interactions between aluminum, phosphorus, and pH in the response of barley to soil acidity. Plant Soil 61: 365-375.

Bachra, B.N. and Van Harskamp, G.A. 1970. The effect of polyvalent metal ions on the stability of a buffer system for calcification in vitro. Calcified Tiss. Res. 4: 359-365.

Baes, C.F., Jr. and Mesmer, R.E. 1976. The hydrolysis of cations. John Wiley-Interscience, New York. 496 pp.

Bailey, R.A., Clarke, H.M., Ferris, J.P., Krause, S. and Strong, R.L. 1978. Chemistry of the environment. Academic Press, New York.

Baker, J.P. 1981. Aluminium toxicity to fish as related to acid precipitation and Adirondack surface water chemistry. Ph. D. Thesis, Cornell University, Ithaca, New York.

Baker, J.P. and Schofield, C.L. 1980. Aluminum toxicity to fish as related to acid precipitation and Adirondack surface water quality. Proc. Int. Conf. Ecological Impact Acid Precipitation, Norway. Edited by D. Drablos and A. Tollan. SNSF Project. pp. 292-293.

Baker, J.P. and Schofield, C.L. 1982. Aluminum toxicity to fish in acidic waters. Water Air Soil Pollut. 18: 289-309.

Bankston, D.C., Humphris, S.E. and Thompson, G. 1979. Major and minor oxide and trace element determination in silicate rocks by direct current plasma optical emission echelle spectrometry. Anal. Chem. 51(8): 1218-1225.

Barko, J.W. 1982. Influence of potassium source (sediment vs. open water) and sediment composition on the growth and nutrition of a submersed freshwater macrophyte (Hydrilla verticillata) (l.f.) (Royle). Aquat. Bot. 12: 157-172.

Bartuska, A.M. and Ungar, I.A. 1980. Elemental concentrations in plant tissues as influenced by low pH soils. Plant Soil 55: 157-161.

Baumgartl, S., Ryder, P.L. and Buehler, H.E. 1973. Detection limits of thin coatings measured with the electron microprobe. Z. Metallk. 64(9): 655-661.

Becker, A.J., Jr. and Keller, E.C., Jr. 1973. The effects of iron and sulfate compounds on the growth of Chlorella. Proc. W. Va. Acad. Sci. 45: 127.

Behr, G. and Burton, P. 1973. Heart-muscle magnesium. Lancet 2: 450.

Benes, P. and Steinnes, E. 1975. Migration forms of trace elements in natural fresh waters and the effect of the water storage. Water Res. 9: 741-749.

Berg, W.A. 1978. Aluminum and manganese toxicities in acid coal mine wastes. In Environmental management of mineral wastes. Edited by G.T. Goodman and M.J. Chadwick. Sijthoff and Noordhoff, Amsterdam.

Berlyne, G.M., Yagil, R., Ben-Ari, J., Weinberger, G., Knopf, E. and Danovitch, G.M. 1972. Aluminum toxicity in rats. Lancet 1: 564-568.

Bertrand, D. and de Wolf, A. 1966. Aluminum as a dynamic oligoelement for higher plants. C.R. Acad. Sci. Paris 262: 479.

Best, M.D. and Peverly, J.H. 1981. Water and sediment chemistry and elemental composition of macrophytes. Proc. Int. Symp. on Acidic Precipitation and Fishery Impacts in N.E. North America. N.E. Div. Am. Fish. Soc., Cornell Univ., Ithaca, New York, Aug. 2-5.

Biesinger, K.E. and Christensen, G.M. 1972. Effects of various metals on survival, growth, reproduction and metabolism of Daphnia magna. J. Fish. Res. Board Can. 29: 1691-1700.

Bjor, K. and Teigen, O. 1980. Effects of acid precipitation on soil and forest. 6. Lysimeter experiment in greenhouse. Proc. Int. Conf. Ecological Impact Acid Precipitation, Norway. Edited by D. Drablos and A. Tollan. SNSF Project. pp. 200-201.

Blair, A.W. and Prince, A.L. 1923. Studies of the toxic principles of soils. Soil Sci. 15: 109-29.

Blamey, F.P.C., Edwards, D.G. and Asher, C.J. 1983. Effects of aluminum, OH:Al, and P:Al molar ratios, and ionic strength on soybean root elongation in solution culture. Soil Sci. 136: 197-207.

Blancher, R.W. and Scrivener, C.L. 1972. Aluminum and iron ion products in acid extracts of samples from various depths in a Menfro soil. Soil Sci. Soc. Am. Proc. 36: 897-901.

Bleiwas, A.H. 1983. Plankton communities and zooplankton grazing rates in some acidic and circumneutral Ontario lakes. MSc Thesis, Univ. of Toronto, Toronto, Ontario.

Bloom, P.R., Weaver, R.M. and McBride, M.B. 1978. The spectrophotometric and fluorometric determination of aluminum with 8-hydroxyquinoline and butyl acetate extraction. Soil Sci. Soc. Am. J. 42(5): 713-716.

Bloom, P.R., McBride, M.B. and Weaver, R.M. 1979. Aluminum organic matter in acid soils: buffering and solution aluminum activity. Soil Sci. Soc. Am. J. 43: 488-493.

Bloom, W.L. and Flinchum, D. 1960. Osteomalacia with pseudofractures caused by the ingestion of aluminum hydroxide. J. Am. Med. Assoc. 174: 1327-1330.

Blotcky, A.J., Hobson, D., Leffler, J.A., Rack, E.P. and Recker, R.R. 1976. Determination of trace aluminum in urine by neutron activation analysis. Anal. Chem. 48(7): 1084-1088.

Bohm, E.L. 1972. Concentration and distribution of Al, Fe, and Si in the calcareous alga Halimeda opuntia (L.) (chlorophyta, udoteaceae). Int. Rev. Gesamten Hydrobiol. 57: 631-637.

Böhm-Tüchy, E. 1960. Plasmalemma and the action of aluminum salts. Protoplasma 52: 108.

Bolt, B.W. and Bruggenwert, M.G.M. 1976. Soil chemistry. A. Basic elements. In Developments in soil science. Vol. 5A. Elsevier, Amsterdam.

Bormann, F.H. and Likens, G.E. 1979. Pattern and process in a forested ecosystem. Springer-Verlag, New York.

Bormann, F.H., Likens, G.E., Siccama, T.G., Pierce, R.S. and Eaton, J.S. 1974. The export of nutrients and recovery of stable conditions following deforestation at Hubbard Brook. Ecol. Monogr. 44: 255-277.

Bottero, J.Y, Cases, J.M., Fiessingen, F. and Poirier, J.E. 1980. Studies of hydrolyzed aluminum chloride solutions. 1. Nature of aluminum species and composition of aqueous solutions. J. Phys. Chem. 84(22): 2933-2939.

Boulton, R.B. and Ewan, G.T. 1977. Simultaneous analysis of light elements using prompt nuclear reaction gamma rays. Anal. Chem. 49(9): 1297-1304.

Bouma, D., Dowling, E.J. and David, D.J. 1981. Relations between plant aluminum content and the growth of lucerne and subterranean clover: their usefulness in the detection of aluminum toxicities. Aust. J. Exp. Agric. Anim. Husb. 21: 311-317.

Bouton, J.H., Hammel, J.E. and Sumner, M.E. 1982. Alfalfa, Medicago sativa L., in highly weathered, acid soils. IV. Root growth into acid subsoil of plants selected for acid tolerance. Plant Soil 65: 187-192.

Bowdler, N.C., Beasley, D.S., Fritze, E.C., Goulette, A.M., Hatton, J.D., Hession, J., Ostman, D.L., Rugg, D.J. and Schmittdiel, C.J. 1979. Behavioral effects of aluminum ingestion on animal and human subjects. Pharmacol. Biochem. Behav. 10(4): 505-512.

Bowen, H.J.M. 1979. Environmental chemistry of the elements. Academic Press, New York.

Bower, N.W. and Ingle, J.D. 1979. Precision of flame atomic absorption spectrometric measurements of aluminum, chromium, cobalt, europium, lead, manganese, nickel, potassium, selenium, silicon, titanium and vanadium. Anal. Chem. 51(1): 72-76.

Boyce, B.F., Fell, G.S., Elder, H.Y., Junor, B.J., Elliot, H.L., Beastall, G., Fogelman, I. and Boyle, I.T. 1982. Hypercalcaemic osteomalacia due to aluminum toxicity. Lancet 2: 1009-1012.

Boyd, C.E. and Lawrence, J.M. 1967. The mineral composition of several freshwater algae. Proc. 12th Annu. Conf. S.E. Assoc. Game Fish Comm. pp. 413-424.

Braekke, F.H. (Editor.) 1976. Impact of acid precipitation on forests and freshwater ecosystems in Norway. SNSF Res. Rep. 6/76.

Breemen, N. van. 1973. Dissolved aluminum in acid sulfate soils and in acid mine waters. Soil Sci. Soc. Am. Proc. 37: 694-697.

Bringmann, G. and Kuhn, R. 1959. The toxic effects of wastewater on aquatic bacteria, algae, and small crustaceans. Gesund. Ing. 80: 115.

Brodie, K.G. and Liddell, P.R. 1980. Zeeman effect in flame atomic absorption spectrometry. Anal. Chem. 52(7): 1059-1064.

Bronsted, J.N. and Volqvartz, K. 1928. Über die Säuredissoziation von Aquoionen II. Z. Physik. Chem. 134: 97-134.

Brosset, C. 1952. On the reactions of the aluminum ion with water. Acta Chem. Scand. 6: 910-940.

Brosset, C., Biedermann, G. and Sillén, L.G. 1954. Studies on the hydrolysis of metal ions. XI. The aluminum ion, Al^{3+}. Acta Chem. Scand. 8: 1917-1926.

Brown, D.J.A. 1981. The effects of various cations on the survival of brown trout, *Salmo trutta*, at low pH's. J. Fish Biol. 18: 31-40.

Brown, D.J.A. 1983. Effects of calcium and aluminum concentration on the survival of brown trout (*Salmo trutta*) at low pH. Bull. Environ. Contam. Toxicol. 30: 582-587.

Brown, G. and Newman, A.C.D. 1973. The reactions of soluble aluminum with montmorillonite. J. Soil Sci. 24(3): 339-354.

Brown, J., Grant, C.L., Ugolini, F.C. and Tedrow, J.C.F. 1962. Mineral composition of some drainage waters from arctic Alaska. J. Geophys. Res. 67: 2447-2453.

Bruce, M.A. and Fraser, H. 1975. Amyloid plaques in the brains of mice infected with scrapie. Morphological variation and standing properties. Neuropathol. Appl. Neurobiol. 1: 189.

Brun, A. and Dictor, N. 1981. Senile plaques and tangles in dialysis dementia. Acta Pathol. Microbiol. Scand. (Sect. 1) 89: 193-198.

Brunskill, G.J., Povoledo, D., Graham, B.W. and Stainton, M.P. 1971. Chemistry of surface sediments of sixteen lakes in the Experimental Lakes Area, Northwestern Ontario. J. Fish. Res. Board Can. 28: 277-294.

Brusewitz, S. 1984. Aluminum. University of Stockholm, Institute of Physics Report (USIP) 84-11. 138 pp.

Buchanan, M.R.C., Ihle, B.U. and Dunn, C.M. 1981. Hemodialysis related osteomalacia: A staining method to demonstrate aluminum. J. Clin. Pathol. 34: 1352-1354.

Buono, J.A., Buono, J.C. and Fasching, J.L. 1977. Simultaneous determination of Al, V, Mn and Cu from neutron-activated saline matrice by precipitation with poly-5-vinyl-8-hydroxyquinoline. J. Radioanal. Chem. 36: 353-358.

Burman, J.-O. and Bostrom, K. 1979. Comparison of different plasma excitation and calibration methods in the analysis of geological materials by optical emission spectrometry. Anal. Chem. 51(4): 516-520.

Burnatowska-Hledin, M.A. and Mayor, G.H. 1982. The effect of aluminum (Al) loading on specific tissue calcium (Ca) and magnesium (Mg) concentrations in normal rats. Clin. Res. 30: A741.

Burrows, W.D. 1977. Aquatic aluminum: Chemistry, toxicology and environmental prevalence. CRC Crit. Rev. Environ. Control 7(2): 167-216.

Cahill, T.A., Sommerville, R. and Flocchini, R. 1971. Elemental analysis of smog by charged particle beams: elastic scattering and x-ray fluorescence. In Nuclear methods in environmental research. Proc. Am. Nucl. Soc., Univ. of Missouri-Columbia, Aug. 23-24, 1971. Edited by J.R. Vogt, T.F. Parkinson and R.L. Carter. Published by Office of Conferences and Short Courses, Univ. of Missouri-Columbia.

Cam, J.M., Luck, V.A., Eastwood, J.B. and deWardener, H.E. 1976. The effect of aluminum hydroxide orally on calcium, phosphorus and aluminum metabolism in normal subjects. Clin. Sci. Mol. Med. 51: 407-419.

Campbell, L.G. and Lafever, H.N. 1981. Heritability of aluminum tolerance in wheat. Cereal Res. Commun. 9: 281-287.

Campbell, P.G.C., Bisson, M., Bougie, R., Tessier, A. and Villeneuve, J.P. 1983. Speciation of aluminum in acidic freshwaters. Anal. Chem. 55(14): 2246-2252.

Campbell, P.G.C., Bougie, R., Tessier, A. and Villeneuve, J.P. 1984. Aluminum speciation in surface waters on the Canadian Pre-Cambrian Shield. Verh. Int. Ver. Limnol. 22: 371-375.

Campbell, R.S. and Lind, O.T. 1969. Water quality and aging of strip-mine lakes. J. Water Pollut. Control Fed. 41: 1943.

Campbell, R.S., Lind, O.T., Geiling, W.T. and Harp, G.L. 1964. Recovery from acid pollution in shallow strip-mine lakes in Missouri. Proc. 19th Ind. Waste Conf., May 5-7, 1964, Purdue Univ., Lafayette, Indiana. Eng. Ext. Ser. No. 117. pp. 17-26.

Campbell, W.J., Spano, E.F. and Green, T.E. 1966. Micro and trace analysis by a combination of ion exchange resin-loaded papers and x-ray spectrography. Anal. Chem. 38(8): 987-996.

Cano-Pavon, J.M., Trujillo, M.L. and Garcia de Torres, A. 1980. 3-hydroxypyridine-2-aldehyde 2-pyridylhydrazone as an analytical reagent. Anal. Chim. Acta 117: 319-327.

Carignan, R. and J. Kalff. 1980. Phosphorus sources for aquatic weeds: Water or sediments? Science 207: 987-989.

Carrière, D., Peakall, D.B., Fischer, K.L. and Angehrn, P. 1986. Effects of dietary aluminum sulphate on reproductive success and growth of ring doves (*Streptopelia risoria*). Can. J. Zool. (In press.)

Carron, J.M. and Aspila, K.I. 1976. Interlaboratory quality control studies nos. 12 and 13: aluminum, cadmium, chromium, cobalt, copper, lead, iron, manganese, nickel and zinc. Canada Centre for Inland Waters, Burlington, Ontario. 20 pp.

Carvalho, M.M. de, Bushby, H.V.A. and Edwards, D.G. 1981a. Survival of *Rhizobium* in nutrient solutions containing aluminum. Soil Biol. Biochem. 13: 541-542.

Carvalho, M.M. de, Edwards, D.G., Andrew, C.S. and Asher, C.J. 1981b. Aluminum toxicity, nodulation, and growth of *Stylosanthes* species. Agron. J. 73: 261-265.

Carvalho, M.M. de, Edwards, D.G., Asher, C.J. and Andrew, C.S. 1982a. Effects of aluminum on nodulation of two *Stylosanthes* species grown in nutrient solution. Plant Soil 64: 141-152.

Carvalho, M.M. de, Asher, C.J., Edwards, D.G. and Andrew, C.S. 1982b. Lack of effect of aluminum concentrations on nitrogen fixation by nodulated *Stylosanthes* species. Plant Soil 66: 225-231.

Cecil, H.C., Bitman, J., Fries, G.F., Harris, S.J. and Lillie, R.J. 1973. Changes in egg shell quality and pesticide content of laying hens or pullets fed DDT in high or low calcium diets. Poult. Sci. 52: 648-653.

Cercasov, V. 1979. Method for simultaneous determination of Al and Si in atmospheric aerosols by 14 MeV neutron activation analysis. J. Radioanal. Chem. 52(2): 399-410.

Chadwick, M.J. and Lindman, N. (Editors.) 1982. Environmental implications of expanded coal utilization. Pergamon Press, Oxford. 283 pp.

Chakrabarti, C.L., Hamed, H.A., Wan, C.C., Li, W.C., Bertels, P.C., Gregoire, D.C. and Lee, S. 1980. Capacitive discharge heating in graphite furnace atomic absorption spectrometry. Anal. Chem. 52: 167-176.

Chen, D.T.Y. 1973. Solubility products of aluminum hydroxide in various ionic solutions. Can. J. Chem. 51: 3528-3533.

Christophersen, N. and Wright, R.F. 1980. Sulfate at Birkenes, a small forested catchment in southernmost Norway. Proc. Int. Conf. Ecological Impact Acid Precipitation, Norway. *Edited by* D. Drablos and A. Tollan. SNSF Project. pp. 286-287.

Christophersen, N. and Wright, R.F. 1981. Sulfate budget and a model for sulfate concentrations in stream water at Birkenes, a small forested catchment in southernmost Norway. Water Resour. Res. 17(2): 377-389.

Christophersen, N., Seip, H.M. and Wright, R.F. 1982. A model for streamwater chemistry at Birkenes, Norway. Water Resour. Res. 18(4): 977-996.

Clark, J.S. and Nichol, W.E. 1966. The lime potential base saturation relations of acid surface horizons of mineral and organic soils. Can. J. Soil Sci. 46: 281-285.

Clark, K.L. and LaZerte, B.D. 1985. A laboratory study of the effects of aluminum and pH on amphibian eggs and tadpoles. Can. J. Fish. Aquat. Sci. 42: 1544-1551.

Clark, K.L. and Hall, R.J. 1985. A study of the effects of pH and aluminum on amphibian eggs and larvae. Can. J. Zool. 63: 116-123.

Clark, R.B. 1977. Effect of aluminum on the growth and mineral elements of Al-tolerant and Al-intolerant corn. Plant Soil 47: 653-662.

Clarkson, D.T. 1966. Aluminum tolerance in species within the genus Agrostis. J. Ecol. 54: 167-178.

Clarkson, D.T. 1969. Metabolic aspects of aluminum toxicity and some possible mechanisms for resistance. In Ecological aspects of the mineral nutrition of plants. Edited by I.H. Rorison. Blackwell Sci. Publ., Oxford. pp. 381-397.

Clarkson, E.M., Luck, V.A., Hynson, W.V., Bailey, R.R., Eastwood, J.B., Clements, J.S., O'Riordan, J.L.H. and Wardener, H.E. 1972. The effect of aluminum hydroxide on calcium, phosphorus and aluminum balances, the serum parathyroid hormone concentration and the aluminum content of bone in patients with chronic renal failure. Clin. Sci. 43: 519-531.

Clymo, R.S. 1962. An experimental approach to part of the calcicole problem. J. Ecol. 50: 707-731.

Coburn, J.W., Brickman, A.S., Sherrard, D.J., Singer, F.R., Wong, E.G.C., Baylink, D.J. and Norman, A.W. 1977. Use of 1,25(OH)2-vitamin D3 to separate "types" of renal osteodystrophy. Proc. Eur. Dial. Transplant Assoc. 14: 442-450.

Cochran, M., Platts, M.M., Moorhead, P.J. and Buxton, A. 1981. Spontaneous hypercalcemia in maintenance dialysis patients: an association with atypical osteomalacia and fractures. Mineral Electrolyte Metab. 5: 280-286.

Collier, R.C., Whetstone, G.W. and Musser, J.J. 1964. Influences of strip mining on the hydrologic environment of parts of Beaver Creek Basin, Ky. U.S. Geol. Surv. Prof. Pap. 427-B. pp. 1955-1959.

Collins, N.C., Zimmerman, A.P. and Knoechel, R. 1981. Comparisons of benthic infauna and epifauna biomasses in acidified and non-acidified Ontario lakes. In Effects of acidic precipitation on benthos. Edited by R. Singer. North American Benthological Society, Springfield, Illinois. pp. 35-48.

Columbera, P.M., Posner, A.M. and Quick, J.P. 1971. The adsorption of aluminum from hydroxy-aluminum solutions onto Fithian illite. J. Soil Sci. 22: 118-128.

Confer, J.L., Kaaret, T. and Likens, G.E. 1983. Zooplankton diversity and biomass in recently acidified lakes. Can. J. Fish. Aquat. Sci. 40: 36-42.

Conner, S.D. 1916. Acid soils and effect of acid phosphate and other fertilizers upon them. J. Ind. Eng. Chem. 8: 35-40.

Conner, S.D. 1921. Liming in its relation to injurious inorganic compounds in the soils. J. Am. Soc. Agron. 13: 113-124.

Cooke, N., Teitelbaum, S. and Avioli, L.V. 1978. Antacid-induced osteomalacia and nephrolithiasis. Arch. Intern. Med. 138: 1007-1009.

Copeland, R.A. and Ayers, J.C. 1972. Trace element distributions in water, sediment, phytoplankton, zooplankton and benthos of Lake Michigan. Environmental Research Group, Inc., Ann Arbor, Michigan.

Coulter, B.S. 1969. The chemistry of hydrogen and aluminum ions in soils, clay minerals and resins. Soils Fert. 32: 215-223.

Cournot-Witmer, G., Zingraff, J., Bourdon, R., Drueke, T. and Balsan, S. 1979. Aluminum and dialysis bone disease. Lancet 2: 795-796.

Cournot-Witmer, G., Zingraff, J., Plachot, J.J., Escaig, F., Lefevre, R., Boumati, P., Bourdeau, A., Garabedian, M., Galle, P., Boudon, R., Drueke, T. and Balsan, S. 1981. Aluminum localization in bone from hemodialyzed patients: relationship to matrix mineralization. Kidney Int. 20: 375-385.

Cowgill, U.M. 1973. Biogeochemistry of rare-earth elements in aquatic macrophytes of Linsley Pond, North Branford, Connecticut. Geochim. Cosmochim. Acta 37: 2329-2345. (Cited by Hutchinson 1975.)

Cowling, E. 1983. Personal communication. School of Forest Resources, North Carolina State Univ., Raleigh, North Carolina.

Cox, G.J., Dodds, H.L., Wigman, H.B. and Murphy, F.J. 1931. The effects of high doses of aluminum and iron on phosphorus metabolism. J. Biol. Chem. 92: 11-12.

Cox, R.M. and Hutchinson, T.C. 1980. Multiple metal tolerances in the grass Deschampsia caespitosa (L.) Beauv. from the Sudbury smelting area. New Phytol. 84: 631-647.

Crapper, D.R. 1974. Dementia: recent observation on Alzheimer's disease and experimental aluminum encephalopathy. In Frontiers of neurology and neuroscience research. Edited by P.M. Seeman and G.M. Brown. Univ. of Toronto Press, Toronto, Ontario. pp. 97-111.

Crapper, D.R. and Dalton, A.J. 1973. Alterations in short-term retention, conditioned avoidance response acquisition and motivation following aluminum induced neurofibrillary degeneration. Physiol. Behav. 10: 925-933.

Crapper, D.R. and De Boni, U. 1977. Aluminum and the genetic apparatus in Alzheimer's disease. In The aging brain and senile dementia. Edited by K. Nandy and I. Sherwin. Plenum Press, New York and London. pp. 229-246.

Crapper, D.R., Krishnana, S.S. and Quittkat, S. 1976. Aluminum, neurofibrillary degeneration and Alzheimer's disease. Brain 99: 67-80.

Crapper, D.R., Karlik, S. and De Boni, U. 1978. Aluminum and other metals in senile (Alzheimer) dementia. In Alzheimer's disease: Senile dementia and related disorders (aging). Edited by R. Katzman, R.D. Terry and K.L. Bicks. Raven Press, New York. pp. 471-485.

Crapper, D.R., Quittkat, S., Krishnan, S.S., Dalton, A.J. and De Boni, U. 1980. Intranuclear aluminum content in Alzheimer's disease. Dialysis encephalopathy and experimental aluminum encephalopathy. Acta Neuropathol. 50(1): 19-24.

Crapper McLachlan, D.R., Dam, T.-V., Farnell, B.J. and Lewis, P.N. 1983. Aluminum inhibition of ADP-ribosylation in vivo and in vitro. Neurobehav. Toxicol. Teratol. 5: 645-647.

Creed, I. 1984. Personal communication. Institute for Environmental Studies, Univ. of Toronto, Toronto, Ontario.

Cronan, C.S. and Schofield, C.L. 1979. Aluminum leaching response to acid precipitation: effects on high-elevation watersheds in the Northeast. Science 204: 304-306.

Cuisinier-Gleizes, P., George, A., Guillano, C. and Mathieu, H. 1971. Stimulation of bone resorption by phosphorus deprivation in the rat. Isr. J. Med. Sci. 7 (3): 355.

Curtis, W.R. 1972. Chemical changes in streamflow following surface mining in Eastern Kentucky. In Proc. 4th Symp. on Coal Mine Drainage Research. Mellon Inst., Pittsburgh, April 26-27.

Dagnall, R.M., West, T.S. and Whitehead, P. 1973. The determination of volatile metal chelates by using a microwave-excited emissive detector. Analyst 98: 647-654.

Dalal, R.C. 1975. Hydrolysis products of solution and exchangeable aluminum in acidic soils. Soil Sci. 119: 127-131.

Dams, R., Rahn, K. and Winchester, J.W. 1970. Non-destructive neutron activation analysis of air pollution particulates. Anal. Chem. 42: 86.

Dams, R., Rahn, K., Nifong, G., Robbins, J. and Winchester, J. 1971. Nondestructive multielement neutron activation analysis of air pollution particulates. In Nuclear methods in environmental research. Edited by J. Vogt, T.F. Parkinson and R.L. Carter. Office of Conferences and Short Courses, Univ. of Missouri-Columbia. pp. 8-15.

Danielsson, L.G. 1982. On the use of filters for distinguishing between dissolved and particulate fractions in natural waters. Water Res. 16(2): 179-182.

David, D.J. 1980. Determination of aluminum in plant material by atomic absorption spectrophotometry. Commun. Soil Sci. Plant Anal. 11(2): 189-199.

Davies, P. and Maloney, A.J.F. 1976. Selective loss of central cholinergic neurons in Alzheimer's disease. Lancet 2: 1403.

De Boni, U., Scott, J.W. and Crapper, D.R. 1974. Intracellular aluminum binding; a histochemical study. Histochemistry 40: 31-37.

De Boni, U., Seger, M. and McLachlan, D.R.C. 1980. Functional consequences of chromatin bound aluminum in cultured human cells. Neurotoxicology 1(4): 65-82.

Deconninck, G. and Demortimer, G. 1972. Quantitative analysis of aluminum by prompt nuclear reaction. J. Radioanal. Chem. 12: 189-208.

De Hek, H., Stol, R.J. and De Bruyn, P.L. 1978. Hydrolysis-precipitation studies of aluminum (III) solutions. 3. The role of the sulfate ion. J. Colloid Interface Sci. 64(1): 72-89.

Dent, C.E. and Winter, C.S. 1974. Osteomalacia due to phosphate depletion from excessive aluminum hydroxide ingestion. Br. Med. J. 23: 551-552.

Dezelic, N., Bilinski, H. and Wolf, R.H.H. 1971. Precipitation and hydrolysis of metallic ions. IV. Studies on the solubility of aluminum-hydroxide in aqueous solution. J. Inorg. Nucl. Chem. 33: 791-798.

Dickson, W. 1978a. Some effects of the acidification of Swedish lakes. Verh. Int. Ver. Limnol. 20: 851-856.

Dickson, W. 1978b. Liming. In Limnological aspects of acid precipitation. Edited by G.R. Hendrey. Proc. Int. Workshop, Sagamore Lake Conference Center, Sept. 25-28. pp. 37-41.

Dickson, W. 1980. Properties of acidified waters. Proc. Int. Conf. Ecological Impact Acid Precipitation, Norway. Edited by D. Drablos and A. Tollan. SNSF Project. pp. 75-83.

Dillard, J.G., Seals, R.D. and Wightman, J.P. 1980. Electron spectroscopy for chemical analysis (ESCA) study of aluminum-containing atmospheric particles. Atmos. Environ. 14: 129-135.

Dillon, P.J., Yan, N.D., Scheider, W.A. and Conroy, N. 1979. Acidic lakes in Ontario, Canada: Characterization, extent and responses to base and nutrient additions. Arch. Hydrobiol. Beih. Ergebn. Limnol. 13: 317-336.

Dodge, C.D. and Hiatt, A.J. 1972. Relationship of pH to ion uptake imbalance by varieties of wheat (Triticum vulgare L.). Agron. J. 64: 476-477.

Driscoll, C. 1978. Aluminium chemistry in dilute waters. In Limnological aspects of acid precipitation. Edited by G.R. Hendrey. Proc. Int. Workshop, Sagamore Lake Conference Center, Sept. 25-28. pp. 6-12.

Driscoll, C.T. 1980. Chemical characterization of some dilute acidified lakes and streams in the Adirondack region of New York State. PhD Thesis, Cornell Univ., Ithaca, New York. 329 pp.

Driscoll, C.T. 1985. In preparation. Dep. of Civil Engineering, Syracuse Univ., Syracuse, New York.

Driscoll, C.T., Baker, J.P., Bisogni, J.J. and Schofield, C.L. 1984. Aluminum speciation and equilibria in dilute acidic surface water of the Adirondack region of New York State. In Geological aspects of acid deposition. Edited by O.P. Bricker. Butterworth Publ., Boston. pp. 55-75.

Drueke, T. 1980. Dialysis osteomalacia and aluminum intoxication. Nephron 26: 207-210.

Duckett, S. and Galle, P. 1976. Mise en evidence de l'aluminium dans les plaques seniles de la maladie d'Alzheimer: étude à la microsonde de Castaing. C.R. Acad. Sci. Paris 282: 393-395.

Duckett, S., Galle, P., Escourolle, R. and Grey, F. 1976. Presence d'aluminium et de magnesium au niveau des arteres et du parenchyme cerebral de malades atteints de syndrome striatonigre: étude à la microsonde de Castaing. C.R. Acad. Sci. Paris 282: 2115-2117.

Duncan, R.R. 1981. Variability among sorghum genotypes for uptake of elements under acid soil field conditions. J. Plant Nutr. 4: 21-32.

Dunkley, G.C. 1982. Aluminum reduction in bladder cancer. Can. Med. Assoc. J. 126: 1026.

Duvick, D.N., Kleese, R.A. and Frey, N.M. 1981. Breeding for tolerance of nutrient imbalances and constraints to growth in acid, alkaline and saline soils. J. Plant Nutr. 4(2): 111-129.

Eaton, J.S. 1983. Personal communication. Institute of Environmental Studies, The New York Botanical Garden, Millbrook, New York.

Ebeling, G. 1928. Toxicity of some heavy metal salts. Wasser Abwasser 26: 95.

Ebner, K., Liss, L., Couri, D. and Cho, M. 1975. Relationship between the neurofibrillary tangles, neuroaxonal degeneration, aluminum level and clinical symptomatology. Fed. Proc. Fed. Am. Soc. Exp. Biol. 34(3): 849.

Eggimann, D.W. and Betzer, P.R. 1976. Decomposition and analysis of refractory oceanic suspended materials. Anal. Chem. 48(6): 886-890.

Eisenreich, S.J., Thornton, J.D., Munger, J.W. and Gorham, E. 1980. Impact of land-use on the chemical composition of rain and snow in northern Minnesota. Proc. Int. Conf. Ecological Impact Acid Precipitation, Norway. Edited by D. Drablos and A. Tollen. SNSF Project. pp. 110-111.

Electric Power Research Institute. 1983. The integrated lake-watershed acidification study. Vol I. Model principles and applications procedures. EPRI EA-3221.

Elliott, H.L. and MacDougall, A.I. 1978. Aluminum studies in dialysis encephalopathy. Proc. Eur. Dial. Transplant Assoc. 15: 157-163.

Elliott, H.L. and MacDougall, A.I. 1980. Dialysis encephalopathy - evidence implicating aluminum. Dial. Transplant 9(11): 1027-1030.

Elliott, H.L., MacDougall, A.I. and Fell, G.S. 1978a. Aluminum toxicity syndrome. Lancet 1: 1203.

Elliott, H.L., MacDougall, A.I., Fell, G.S. and Gardiner, P.H.E. 1978b. Plasmapheresis, aluminum and dialysis dementia. Lancet 2: 1255.

Ellis, H.A., Pierides, A.M., Feest, T.G., Ward, M.K. and Ker, D.N.S. 1977. Histopathology of renal osteodystrophy with particular reference to the effects of 1-α-hydroxyvitamin D-3 in patients treated by long-term hemodialysis. Clin. Endocrinol. (Oxford) 7 (Suppl.): 31S-38S.

Ellis, H.A., McCarthy, J.H. and Herrington, J. 1979. Bone aluminum in haemodialysed patients and in rats injected with aluminum chloride: relationship to impaired bone mineralization. J. Clin. Pathol. 32: 832-844.

Ellis, K.M. and Chattopadhyay, A. 1979. Multielement determination in estuarine suspended particulate matter by instrumental neutron activation analysis. Anal. Chem. 51(7): 942-947.

Ellis, M.M. 1937. Detection and measurement of stream pollution. Bull. U.S. Bur. Fish. 48(22): 365.

Epstein, M.S., Rains, T.C., Brady, T.J., Moody, J.R. and Barnes, I.L. 1978. Determination of several trace metals in simulated fresh water by graphite furnace atomic emission spectrometry. Anal. Chem. 50(7): 874-880.

Eroshenko, P.V. and Place, T.A. 1978. Variation in dimensions and shell weights of eggs collected from Japanese quail fed kepone with different level calcium diets. Environ. Pollut. 16: 123-127.

Evans, C.E. and Kamprath, E.J. 1970. Lime response as related to per cent Al saturation, solution Al, and organic matter content. Soil Sci. Soc. Am. Proc. 34: 893-896.

Everhart, W.H. and Freeman, R.A. 1973. Effects of chemical variations in aquatic environments. Vol. II. Toxic effects of aqueous aluminum to rainbow trout. EPA-R3-73-011b, Feb. 1973, Office of Research and Monitoring, U.S. Environmental Protection Agency, Washington, D.C.

Farina, M.P.W., Sumner, M.E., Plank, C.O. and Letzsch, W.S. 1980a. Aluminum toxicity in corn at near neutral pH levels. J. Plant Nutr. 2: 683-697.

Farina, M.P.W., Sumner, M.E., Plank, C.O. and Letzsch, W.S. 1980b. Exchangeable aluminum and pH as indicators of lime requirement for corn. Soil Sci. Soc. Am. J. 44: 1036-1041.

Farnell, B.J., De Boni, U. and Crapper McLachlan, D.R. 1982. Aluminum neurotoxicity in the absence of neurofibrillary degeneration in CA1 hippocampal pyramidal neurons in vitro. Exp. Neurol. 78: 241-258.

Fassel, V.A. and Knisseley, R.N. 1974. Inductively coupled plasmas. Anal. Chem. 46(13): 1155A, 1158A, 1162A.

Faucherre, J. 1954. Sur la constitution des ions basiques metalliques. Bull. Soc. Chim. Fr. 21: 253-267.

Fauley, G.B., Freeman, S., Ivy, A.C., Atkinson, A.J. and Wigodsky, H.S. 1941. Aluminum phosphate in the therapy of peptic ulcer. Effect of aluminum hydroxide on phosphate absorption. Arch. Intern. Med. 67: 63-78.

Feder, G.L. 1972. In Geochemical survey of Missouri. Open-file report. U.S. Geological Survey, Denver.

Feinroth, M., Feinroth, M.V., Friedman, E.A. and Berlyne, G.M. 1980. Effect of parathyroid hormone and acute renal failure on aluminum absorption in rat everted gut sacs. Clin. Res. 28: 656 A.

Felsenfeld, A.J., Harrelson, J.M., Gutman, R.A., Wells, S.A. and Drezner, M.K. 1982. Osteomalacia after parathyroidectomy in patients with uremia. Ann. Intern. Med. 96: 34-39.

Fernandez, F.J., Myers, S.A. and Slavin, W. 1980. Background correction in atomic absorption utilizing the Zeeman effect. Anal. Chem. 52: 741-746.

Firestone, M.K., Killham, K. and McColl, J.G. 1983. Fungal toxicity of mobilized soil aluminum and manganese. Appl. Environ. Microbiol. 46: 758-761.

Firschein, H.E. 1969. Phosphate as a regulator of bone collagen and mineral resorption. Fed. Am. Soc. Exp. Biol. Proc. 28: 374. (Abstr. No. 656.)

Fivelstad, S. and Leivestad, H. 1984. Aluminum toxicity to Atlantic salmon (*Salmo salar* L.) and brown trout (*Salmo trutta* L.): Mortality and physiological response. Rep. Inst. Freshwater Res. Drottningholm 61: 69-77.

Fleming, A.L. and Foy, C.D. 1968. Root structure reflects differential tolerance in wheat varieties. Agron. J. 60: 172-176.

Flendrig, J.A., Kruis, H. and Das, H.A. 1976. Aluminum intoxication: the cause of dialysis dementia? Proc. Eur. Dial. Transplant Assoc. 13: 355-364.

Flensburg, T. and Sparling, J.H. 1973. Algal microflora of a string mire in relation to chemical composition of water. Can. J. Bot. 51(4): 743-749.

Fortescue, J.A.C. 1980. Environmental geochemistry. Springer-Verlag, New York.

Fox, R.H. 1979. Soil pH, aluminum saturation, and corn grain yield. Soil Sci. 127: 330-334.

Foy, C.D. 1974. Effects of aluminum on plant growth. *In* The plant root in its environment. *Edited by* E.W. Carson. Univ. of Virginia Press, Charlottesville, Virginia. pp. 601-642.

Foy, C.D. and Fleming, A.L. 1978. The physiology of plant tolerance to excess available aluminum and manganese in acid soils. *In* Crop tolerance to suboptimal land conditions. Soil Science Society of America, Madison, Wisconsin. pp. 301-328.

Foy, C.D. and Gerloff, G.C. 1972. Response of *Chlorella pyrenoidosa* to aluminum and low pH. J. Phycol. 8: 268-271.

Foy, C.D., Armiger, W.H., Briggle, L.W. and Reid, D.A. 1965. Aluminum tolerance of wheat and barley varieties in acid soils. Agron. J. 57: 413-417.

Foy, C.D., Fleming, A.L., Burns, G.R. and Armiger, W.H. 1967a. Characterization of differential aluminum tolerance among varieties of wheat and barley. Soil Sci. Soc. Am. Proc. 31: 513-521.

Foy, C.D., Armiger, W.H., Fleming, A.L., and Lewis, C.F. 1967b. Differential tolerance of cotton varieties to an acid soil high in exchangeable aluminum. Agron. J. 59: 415-418.

Foy, C.D., Fleming, A.L. and Armiger, W.H. 1969a. Differential tolerance of cotton varieties to excess manganese. Agron. J. 61: 690-694.

Foy, C.D., Fleming, A.L. and Armiger, W.H. 1969b. Aluminum tolerance of soybean varieties in relation to calcium nutrition. Agron. J. 61: 505-511.

Foy, C.D., Fleming, A.L. and Gerloff, G.C. 1972. Differential aluminum tolerance in two snapbean varieties. Agron. J. 64: 815-818.

Foy, C.D., Fleming, A.L. and Schwartz, J.W. 1973a. Opposite aluminum and manganese tolerances in two wheat varieties. Agron. J. 65: 123-126.

Foy, C.D., Gerloff, G.C. and Gabelman, W.H. 1973b. Differential effects of aluminum on the vegetative growth of tomato cultivars in acid soil and nutrient solution. J. Am. Soc. Hortic. Sci. 98: 427-432.

Foy, C.D., Lafever, H.N., Schwartz, J.W. and Fleming, A.L. 1974. Aluminum tolerance of wheat cultivars related to region of origin. Agron. J. 66(6): 751-758.

Foy, C.D., Chaney, R.L. and White, M.C. 1978. The physiology of metal toxicity in plants. Annu. Rev. Plant Physiol. 29: 511-566.

Foy, C.D., Oakes, A.J. and Schwartz, J.W. 1979. Adaptation of some introduced *Eragrostis* species to calcareous soil and acid mine spoil. Commun. Soil Sci. Plant Anal. 10: 953-968.

Franco, A.A. and Munns, D.N. 1982. Acidity and aluminum restraints on nodulation, nitrogen fixation, and growth of *Phaseolus vulgaris* in solution culture. Soil Sci. Soc. Am. J. 46: 296-301.

Freedman, B. and Hutchinson, T.C. 1980. Effects of smelter pollutants on forest leaf litter decomposition near a nickel-copper smelter near Sudbury, Ontario. Can. J. Bot. 58: 1722-1736.

Freeman, R.A. and Everhart, W.H. 1971. Toxicity of aluminum hydroxide complexes in neutral and basic media to rainbow trout. Trans. Am. Fish. Soc. 100(4): 644-658.

Frink, C.R. and Peech, M. 1963a. The solubility of gibbsite in aqueous solutions and soil extracts. Inorg. Chem. 2: 473-478.

Frink, C.R. and Peech, M. 1963b. Hydrolysis and exchange reactions of the aluminum ion in hectorite and montmorillonite suspensions. Soil Sci. Soc. Am. Proc. 27: 527-530.

Frink, C.R. and Sawhney, B.L. 1967. Neutralization of dilute aqueous aluminum salt solutions. Soil Sci. 103: 144-148.

Fripiat, J.J., Van Cauwelaert, F. and Bosmans, H.J. 1965. Structure of aluminum cations in aqueous solutions. J. Phys. Chem. 69: 2458-2461.

Furlani, P.R. and Clark, R.B. 1981. Screening *Sorghum bicolor* for aluminum tolerance in nutrient solutions. Agron. J. 73(4): 587-594.

Furr, A.K., Schofield, C.L., Grandolfo, M.C., Hofstader, R.A., Gutenmann, W.H., St. John, L.E., Jr. and Lisk, D.J. 1979. Element content of mosses as possible indicators of air pollution. Arch. Environ. Contam. Toxicol. 8: 335-343.

Gabriëls, R., Van Keirsbulck, W. and Engels, H. 1981. Spectrofluorimetric determination of aluminium in plants, soils, and irrigation waters. Lab. Pract. 30(2): 122-123.

Galle, P. and Guidicelli, C.P. 1982. Toxicité de l'aluminium pour l'hepatocyte. Localisation ultrastructurale et micro-analyse des depots. Nouv. Presse Med. 11(15): 1123-1125.

Galle, P. and Lefevre, R. 1978. Secondary ion emission microanalysis: biomedical applications. Microsc. Acta 1978 (Suppl. 2): 341-354.

Garcia-Bunuel, L., Elliot, D.C. and Bank, N.K. 1980. Apneic spells in progressive dialysis encephalopathy. Arch. Neurol. (Chicago) 37: 594-596.

Gatschke, W. and Gawlik, D. 1980. Simultaneous determination of aluminum and phosphorus by neutron activation analysis. J. Radioanal. Chem. 56(1-2): 203-212.

Gayer, K.H., Thompson, L.C. and Zajicek, B.I. 1958. Solubility of aluminum hydroxide in acidic/basic media at 25°C. Can. J. Chem. 36: 1268-1271.

Gelfant, S. 1963. Inhibition of cell divison: a critical experimental analysis. Rev. Cytol. 14: 249-254.

Gilbert, B.E. and Pember, F.R. 1935. Tolerance of certain weeds and grasses to toxic aluminum. Soil Sci. 39: 425-429.

Gizyn, W.I. 1980. The chemistry and environmental impact of the bituminous shale fires at the Smoking Hills, N.W.T. MSc Thesis, Dep. of Botany, Univ. of Toronto, Toronto, Ontario.

Gjessing, E.T., Henriksen, A., Johannessen, M. and Wright, R.F. 1976. Effects of acid precipitation on freshwater chemistry. In Impact of acid precipitation on forest and freshwater ecosystems in Norway. Edited by F. Braekke. Res. Rep. FR 6/76, Summary report on the research results from phase 1 (1972-1975) of the SNSF Project. pp. 64-85.

Goldschmidt, V.M. 1954. Geochemistry. Clarendon Press, Oxford.

Goodman, F.R. and Weiss, G.B. 1971a. Dissociation by lanthanum of smooth muscle responses to potassium and acetylcholine. Am. J. Physiol. 220: 759-766.

Goodman, F.R. and Weiss, G.B. 1971b. Effects of lanthanum on 45 Ca movements and on contractions induced by norepinephrine, histamine and potassium in vascular smooth muscle. J. Pharmacol. Exp. Ther. 177: 415-425.

Gorham, E. and Gordon, A.C. 1963. Some effects of smelter pollution upon aquatic vegetation near Sudbury, Ontario. Can. J. Bot. 41: 371-378.

Gorham, E. and Tilton, D.L. 1978. The mineral content of Sphagnum fuscum as affected by human settlement. Can. J. Bot. 56: 2755-2759.

Gorsky, J.E. and Dietz, A.A. 1978. Determination of aluminum in biological samples by atomic absorption spectrophotometry with a graphite furnace. Clin. Chem. 24(9): 1485-1490.

Gorsky, J.E., Dietz, A.A., Spencer, H. and Osis, D. 1979. Metabolic balance of aluminum studied in six men. Clin. Chem. 25(10): 1739-1743.

Gosink, T.A. 1975. Rapid simultaneous determination of picogram quantities of aluminum and chromium from water by gas phase chromatography. Anal. Chem. 47(1): 165-167.

Grahn, O.H. 1976. Macrophyte succession in Swedish lakes caused by deposition of airborne acid substances. Proc. 1st Int. Symp. on Acid Precipitation and the Forest Ecosystem. U.S.D.A. For. Serv. Gen. Tech. Rep. NE-23. pp. 519-530.

Grahn, O.H. 1980. Fishkills in two moderately acid lakes due to high aluminum concentrations. Proc. Int. Conf. Ecological Impact Acid Precipitation, Norway. Edited by D. Drablos and A. Tollan. SNSF Project. pp. 310-311.

Grahn, O.H., Hultberg, H. and Landner, L. 1974. Oligotrophication - a self-accelerating process in lakes subjected to excessive supply of acid substances. Ambio 3: 93-94.

Greger, J.L. and Baier, M.J. 1983. Excretion and retention of low or moderate levels of aluminum by human subjects. Food Chem. Toxicol. 21(4): 473-478.

Gresky, A.T., Nurmi, E.O., Forster, D.L., Wischow, R.P. and Savolainen, J.P. 1960. Dibasic aluminum nitrate. U.S. Patent 2,931,706: April 5, 1960.

Grime, J.P. and Hodgson, J.G. 1969. An investigation of the ecological significance of lime chlorosis by means of large scale comparative experiments. *In* Ecological aspects of the mineral nutrition of plants. *Edited by* I.H. Rorison. Blackwell Sci. Publ., Oxford. pp. 67-69.

Grunwald, E. and Fong, D.W. 1969. Acidity and association of aluminum ions in dilute aqueous acid. J. Phys. Chem. 73: 650-653.

Gunn, J.M. and Keller, W. 1980. Enhancement of the survival of rainbow trout (*Salmo gairdneri*) eggs and fry in an acid lake through incubation in limestone. Can. J. Fish. Aquat. Sci. 37(10): 1522-1530.

Gunn, J.M. and Noakes, D.L.G. 1985. Avoidance of low pH and elevated Al concentrations by lake charr (*Salvelinus namaycush*) and brook charr (*S. fontinalis*) yolk sac fry. Poster presentation, Int. Symp. Acidic Precipitation, Sept. 15-20, Muskoka, Ontario.

Guthrie, C.A. 1981. Acclimation of brook trout (*Salvelinus fontinalis*) to acidic water. M.Sc. Thesis, Cornell Univ., Ithaca, New York.

Guthrie, R.K. and Cherry, D.S. 1979. The uptake of chemical elements from coal ash and settling basin effluent by primary producers. 1. Relative concentrations in predominant plants. Sci. Total Environ. 12: 217-222.

Hackett, C. 1962. Stimulative effects of aluminum on plant growth. Nature (London) 195: 471-472.

Hackett, C. 1965. Ecological aspects of the mineral nutrition of *Deschampsia flexuosa* (L.) Trin. II. The effects of Al, Ca, Fe, K, Mn, N, P, and pH on the growth of seedlings and established plants. J. Ecol. 53: 315-333.

Hackett, C. 1967. Ecological aspects of the nutrition of *Deschampsia flexuosa* (L.) Trin. III. Investigation of phosphorus requirement and response to Al in water culture and a study of growth in soil. J. Ecol. 55: 831-840.

Hall, R.J. 1985. Short-term acidification of streams and lakes as a result of snowmelt. IX. Behavioral responses of stream macroinvertebrates to elevated H^+ and Al levels at Dorset and the Experimental Lakes Area (ELA), Ontario, Canada. Poster presentation, Int. Symp. Acidic Precipitation, Sept. 15-20, Muskoka, Ontario.

Hall, J.R. and Likens, G.E. 1981. Chemical flux in an acid-stressed stream. Nature (London) 292: 329-331.

Hall, R.J., Likens, G.E., Fiance, S.B. and Hendrey, G.R. 1980. Experimental acidification of a stream in the Hubbard Brook Experimental Forest, New Hampshire. Ecology 61: 976-989.

Hall, R.J. 1985. Personal communication. Dorset Research Centre, Ontario Ministry of the Environment, Dorset, Ontario.

Hanson, W.D. and Kamprath, E.J. 1979. Selection for aluminum tolerance in soybeans based on seedling-root growth. Agron. J. 71: 581-586.

Hargreaves, J.W., Lloyd, E.J.H. and Whitton, B.A. 1975. Chemistry and vegetation of highly acidic streams. Freshwater Biol. 5: 563-576.

Haridasan, M. 1982. Aluminum accumulation by some cerrado species of central Brasil. Plant Soil 65: 265-273.

Hartell, P.G. and Alexander, M. 1983. Growth and survival of cowpea rhizobia in acid, aluminum-rich soils. Soil Sci. Soc. Am. J. 47: 502-506.

Hartford, W.H. 1942. Chromic acid anodic baths. Interpretation of glass electrode measurements. Ind. Eng. Chem. 34: 920-924.

Hartwell, B.L. and Pember, F.R. 1918. The presence of aluminum as a reason for the difference in the effect of so-called acid soil on barley and rye. Soil Sci. 6: 259-277.

Harvey, H.H. and Lee, C. 1980. Fishes of the La Cloche Mountain lakes of Ontario, 1965-1980. Report to the Ontario Ministry of Natural Resources. 89 pp.

Harvey, H.H. and McArdle, M. 1985. Physiological responses of rainbow trout (Salmo gairdneri) exposed to Plastic Lake inlet and outlet stream water. Poster presentation, Int. Symp. Acidic Precipitation, Sept. 15-20, Muskoka, Ontario.

Harvey, H.H., Pierce, R.C., Dillon, P.J., Kramer, J.R. and Whelpdale, D.M. 1981. Acidification in the Canadian aquatic environment: Scientific criteria for assessing the effects of acidic deposition on aquatic ecosystems. Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. NRCC Publ. No. 18475. 369 pp.

Hausenbuiller, R.L. (Editor.) 1978. Soil science. Wm. C. Brown Co., Dubuque, Iowa.

Haussler, M.R. and McCain, T.A. 1977. Basic and clinical concepts related to vitamin D metabolism and action. N. Engl. J. Med. 297: 974-983.

Hava, M. and Hurwitz, A. 1973. The relaxing effect of aluminum and lanthanum of rat and human gastric smooth muscle *in vitro*. Eur. J. Pharmacol. 22: 156-161.

Havas, M. 1980. A study of the chemistry and biota of acid and alkaline ponds at the Smoking Hills, N.W.T. Ph.D. Thesis, Univ. of Toronto, Toronto, Ontario. 195 pp.

Havas, M. 1985a. Aluminum bioaccumulation and toxicity to *Daphnia magna* in soft water at low pH. Can. J. Fish. Aquat. Sci. 42: 1741-1748.

Havas, M. 1985b. Sites of aluminum deposition in freshwater plants and animals. Poster presentation, Int. Symp. Acidic Precipitation, Sept. 15-20, Muskoka, Ontario.

Havas, M. 1986. Hematoxylin staining technique to locate sites of aluminum binding in aquatic plants and animals. Water Air Soil Pollut. (Submitted.)

Havas, M. and Hutchinson, T.C. 1982. Aquatic invertebrates from the Smoking Hills, N.W.T.: Effect of pH and metals on mortality. Can. J. Fish. Aquat. Sci. 39: 890-903.

Havas, M. and Hutchinson, T.C. 1983. The Smoking Hills: Natural acidification of an aquatic ecosystem. Nature (London) 301: 23-27.

Havas, M. and Likens, G.E. 1985a. Toxicity of aluminum and hydrogen ions to *Daphnia catawba*, *Holopedium gibberum*, *Chaoborus punctipennis*, and *Chironomus anthrocinus* from Mirror Lake, New Hampshire. Can. J. Zool. 63: 1114-1119.

Havas, M. and Likens, G.F. 1985b. Changes in ^{22}Na influx and outflux in *Daphnia magna* in soft water at low pH. Proc. Natl. Acad. Sci. 82: 7345-7349.

Hayden, P.L. and Rubin, A.J. 1974. Systematic investigation of the hydrolysis and precipitation of Al(III). *In* Aqueous environmental chemistry of metals. *Edited by* A.J. Rubin. Ann Arbor Sci. Publ. Inc., Ann Arbor, Michigan. pp. 317-381.

Haynes, R.J. 1984. Effect of lime, silicate, and phosphate applications on the concentrations of extractable aluminum and phosphate in a spodosol. Soil Sci. 138: 8-14.

Haynes, R.J. and Ludecke, T.E. 1981. Effect of lime and phosphorus applications on concentrations of available nutrients and on P, Al, and Mn uptake by two pasture legumes in an acid soil. Plant Soil 62: 117-128.

Helliwell, S., Batley, G.E., Florence, T.M. and Lumsden, B.G. 1983. Speciation and toxicity of aluminum in a model fresh water. Environ. Technol. Lett. 4(3): 141-144.

Helyar, K.R. and Anderson, A.J. 1971. Effects of lime on the growths of five species, on aluminum toxicity, and on phosphorus availability. Aust. J. Agric. Res. 22: 707-721.

Hem, J.D. 1968a. Aluminium species in water. Adv. Chem. Ser. 73: 98-114.

Hem, J.D. 1968b. Graphical methods for studies of aqueous Al hydroxide, fluoride and sulfate complexes. U.S. Geol. Surv. Water Supply Pap. 1827-8.

Hem, J.D. and Roberson, C.E. 1967. Form and stability of aluminum hydroxide complexes in dilute solution. U.S. Geol. Surv. Water Supply Pap. 1827-A.

Hemingway, B.S., Robie, R.A. and Kittrick, J.A. 1978. Revised values for the Gibbs free energy of formation of [$\mathrm{Al(OH)}_4^-$ aq], diaspore, boehmite and bayerite at 298.15 K and 1 bar, the thermodynamic properties of kaolinite to 800 K and 1 bar and the heats of solution of several gibbsite samples. Geochim. Cosmochim. Acta 42: 1533-1543.

Hendrey, G.R. 1982. Effects of acidification on aquatic primary producers and decomposers. *In* Acid rain/fisheries. *Edited by* R.E. Johnson. Am. Fish. Soc., Bethesda, Maryland. pp. 125-135.

Hendrey, G.R. and Vertucci, F.A. 1980. Benthic plant communities in acidic Lake Colden, New York: Sphagnum and the algal mat. Proc. Int. Conf. Ecological Impact Acid Precipitation, Norway. *Edited by* D. Drablos and A. Tollan. SNSF Project. pp. 314-315.

Hendrey, G.R., Baalsrud, K., Traaen, T.S., Laake, M. and Raddum, G. 1976. Acid precipitation: Some hydrobiological changes. Ambio 5: 224-227.

Hendrey, G.R., Yan, N.D. and Baumgartner, K.J. 1980. Responses of freshwater plants and invertebrates to acidification. EPA/OECD Int. Symp. Inland Waters and Lake Restoration, Sept. 8-12. Portland, Maine.

Henriksen, A. and Bergmann-Paulsen, I.-M. 1975. An automatic method for determining aluminum in natural waters. Vatten 31(4): 339-342.

Hileman, B. 1984. Forest decline from air pollution. Environ. Sci. Technol. 18: 8-10.

Hodsman, A.B., Sherrard, D.J., Wong, E.G.C., Brickman, A.S., Lee, D.B., Alfrey, A.C., Singer, F.R., Norman, A.W. and Coburn, J.W. 1981. Vitamin D resistant osteomalacia in hemodialysis patients lacking secondary hyperparathyroidism. Ann. Intern. Med. 94: 629-637.

Hodsman, A.B., Sherrard, D.J., Alfrey, A.C., Ott, S., Brickman, A.S., Miller, N.L., Maloney, N.A. and Coburn, J.W. 1982. Bone aluminum and histomorphometric features of renal osteodystrophy. J. Clin. Endocrinol. Metab. 54(3): 539-546.

Holt, H. and Bruggenwert, M.G.M. 1978. Soil chemistry. A. Basic elements. Elsevier, Amsterdam.

Holtzclaw, K.M., Keech, D.A., Page, A.L., Sposito, G., Ganje, T.J. and Ball, N.B. 1978. Trace metal distributions among the humic acid, the fulvic acid, and precipitable fractions extracted with NaOH from sewage sludges. J. Environ. Qual. 7: 124-127.

Horst, W.J., Wagner, A. and Marschner, H. 1983. Effect of aluminum on root growth, cell-division rate and mineral element contents in roots of Vigna unguiculata genotypes. Z. Pflanzenphysiol. 109: 95-103.

Howeler, R.H. and Cadavid, L.F. 1976. Screening of rice cultivars for tolerance to Al-toxicity in nutrient solutions as compared with a field screening method. Agron. J. 68: 551-555.

Howells, G.D., Brown, D.J.A. and Sadler, K. 1983. Effects of acidity and aluminum on fish productivity. J. Sci. Food Agric. 33(12): 1247.

Hsu, D.Y. and Pipes, W.O. 1972. Modification of technique for determination of aluminum in water by atomic absorption spectrophotometry. Environ. Sci. Technol. 6(7): 645-647.

Hsu, P.H. 1966. Formation of gibbsite from aging hydroxy-aluminum solutions. Soil Sci. Soc. Am. Proc. 30: 173-176.

Hsu, P.H. 1977. Aluminum hydroxides and oxyhydroxides. *In* Minerals in soil environments. *Edited by* J.B. Dixon and S.B. Weed. Soil Science Society of America, Madison, Wisconsin.

Hsu, P.H. and Bates, T.F. 1964a. Fixation of hydroxyaluminum polymers by vermiculite. Soil Sci. Soc. Am. Proc. 28: 763-769.

Hsu, P.H. and Bates, T.F. 1964b. Formation of X-ray amorphous and crystalline aluminum hydroxides. Mineral Mag. 33: 749-768.

Hsu, P.H. and Rich, C.I. 1960. Aluminum fixation in a synthetic cation exchanger. Soi Sci. Soc. Am. Proc. 24: 21-25.

Huang, C.P. 1975. Adsorption of phosphate at the hydrous γ-Al_2O_3-electrolyte interface. J. Colloid Interface Sci. 53: 178-186.

Huber, C.T. and Freiden, E. 1970. The inhibition of ferroxidase by trivalent and other metal ions. J. Biol. Chem. 245: 3979-3984.

Huett, D.O. and Menary, R.C. 1980. Effect of aluminum on growth and nutrient uptake of cabbage, lettuce, and kikuyu grass in nutrient solution. Aust. J. Agric. Res. 31: 749-761.

Hultberg, H. and Andersson, I.B. 1981. Liming of acidified lakes and streams - aspects on induced physical-chemical and biological changes. I.V.L. Publ. B. 621, April.

Hultberg, H. and Grahn, O. 1975. Effects of acid precipitation on macrophytes in oligotrophic Swedish lakes. Proc. 1st. Spec. Symp. on Atmospheric Contribution to the Chemistry of Lake Waters. Int. Assoc. Great Lakes Res., Sept. 28 - Oct. 1. pp. 208-221.

Hultberg, H. and Wenblad, A. 1980. Acid groundwater in southern Sweden. Proc. Int. Conf. Ecological Impact Acid Precipitation, Norway. *Edited by* D. Drablos and A. Tollan. SNSF Project. pp. 220-221.

Humphrys, F.R. and Truman, R. 1964. Aluminium and the phosphorus requirements of *Pinus radiata*. Plant Soil 20(1): 131-134.

Hurwitz, A. 1971. The effects of antacids on gastrointestinal drug absorption. II. Effect of sulfadiazine and quinine. J. Pharmacol. Exp. Ther. 179: 485-489.

Hurwitz, A. and Sheehan, M.B. 1971. The effects of antacids on the absorption of orally administered pentobarbitol in the rat. J. Pharmacol. Exp. Ther. 179: 124-131.

Hutchinson, G.E. 1943. The biogeochemistry of aluminum and of certain related elements. Q. Rev. Biol. 18: 128-153.

Hutchinson, G.E. 1945. Aluminum in soils, plants and animals. Soil Sci. 60: 29-40.

Hutchinson, N.J. and Holtze, K.E. 1985. Biological effects of acidification. XI. Factors influencing the acute lethality of hydrogen and aluminum ion in lake and brook trout. Poster presentation, Int. Symp. Acidic Precipitation, Sept. 15-20, Muskoka, Ontario.

Hutchinson, G.E. (Editor.) 1975. A treatise on limnology. Vol. III. Limnological botany. John-Wiley and Sons, New York. 660 pp.

Hutchinson, T.C. 1980. Effects of acid leaching on cation loss from soils. In Effects of acid precipitation on terrestrial ecosystems. Edited by T.C. Hutchinson and M. Havas. Plenum Press, New York. pp. 481-497.

Hutchinson, T.C. 1983. A historical perspective on the role of aluminum in toxicity of acid soils and lake waters. In Proc. Int. Conf. Heavy Metals in the Environment, Heidelberg, West Germany, September. CEP Consultants, Edinburgh, U.K.

Hutchinson, T.C. and Bozic, L. 1985. Unpublished data. Presented at Int. Symp. on Acid Precipitation, Muskoka, Ontario, Sept. 15-20. Institute for Environmental Studies, Univ. of Toronto, Toronto, Ontario.

Hutchinson, T.C., Nakatsu, C. and Tam, D. 1981. Multiple metal tolerances and co-tolerances in algae. In Proc. Int. Conf. Heavy Metals in the Environment, Amsterdam, Sept. CEP Consultants, Edinburgh. pp. 300-304.

Hüttermann, A. 1984. Solid phase solution - root interactions in soils subjected to acid deposition. Phil. Trans. R. Soc. London B 305: 353.

Hydes, D.J. and Liss, P.S. 1976. Fluorimetric method for the determination of low concentrations of dissolved aluminum in natural waters. Analyst 101(1209): 922-931.

Ihnat, M. 1976. Flame atomic emission spectrometric determination of aluminum in a bovine blood plasma matrix. Anal. Biochem. 73(1): 120-133.

Insogna, K.L., Bordley, D.R., Caro, J.F. and Lockwood, D.H. 1980. Osteomalacia and weakness from excessive antacid ingestion. J. Am. Med. Assoc. 244: 2544-2546.

Ishibashi, N. and Kina, K. 1972. Sensitivity enhancement of the fluorometric determination of aluminum by the use of surfactant. Anal. Lett. 5(9): 637-641.

Ishii, T. 1966. Distribution of Alzheimer's neurofibrillary changes in the brain stem and hypothalamus of senile dementia. Acta Neuropathol. 6: 181-187.

Ishizuka, T. and Uwamino, Y. 1980. Atomic emission spectrometry of solid samples with laser vaporization - microwave induced plasma system. Anal. Chem. 52: 125-129.

Ito, T. and Yui, N. 1953. Hydrolysis constants of aluminum ion in chloride solutions. Chem. Abstr. 48: 5613c.

Ivarson, K.C., Ross, G.J. and Miles, N.M. 1982. Microbiological transformations of iron and sulfur and their applications to acid sulfate soils and tidal marshes. Soil Sci. Soc. Am. Spec. Publ. 10: 57-76.

Jackson, T.A. 1975. Humic matter in natural waters and sediments. Soil Sci. 119: 56-64.

Jackson, T.A. and Schindler, D.W. 1975. The biogeochemistry of phosphorus in an experimental lake environment: Evidence for the formation of humic-metal-phosphate complexes. Verh. Int. Ver. Limnol. 19: 211-221.

Johannessen, M. 1980. Aluminum, a buffer in acidic waters? In Proc. Int. Conf. Ecological Impact Acid Precipitation, Norway. Edited by D. Drablos and A. Tollan. SNSF Project. pp. 222-223.

Johannessen, M. and Joranger, E. 1976. Water chemistry studies in the Fyresdal (Nissedal) watersheds. SNSF Project TN.

John, J. 1971. Californium-252 based system for the automated detection of heavy metals in inland waters. In Nuclear methods in environmental research. Edited by J.R. Vogt, T.F. Parkinson and R.L. Carter. Office of Conferences and Short Courses, Univ. of Missouri-Columbia. pp. 72-85.

Johnson, D.W. 1980. Site susceptibility to leaching by H_2SO_4 in acid rainfall. In Effects of acid precipitation on terrestrial ecosystems. Edited by T.C. Hutchinson and M. Havas. Plenum Press, New York. pp. 525-536.

Johnson, D.W. and Cole, D.W. 1977. Sulfate mobility in an outwash soil in western Washington. Water Air Soil Pollut. 7(4): 489-495.

Johnson, D.W. and Cole, D.W. 1980. Anion mobility in soils: relevance to nutrient transport from forest ecosystems. Environ. Int. 3(1): 79-90.

Johnson, D.W. and Henderson, G.S. 1979. Sulfate adsorption and sulfur fractions in a highly weathered soil under a mixed deciduous forest. Soil Sci. 128(1): 34-40.

Johnson, D.W. and Todd, D.E. 1983. Relationships among iron, aluminum, carbon, and sulfate in a variety of forest soils. Soil Sci. Soc. Am. J. 47: 792-800.

Johnson, G.W., Taylor, H.E. and Skogerboe, R.K. 1979. Evaluation of solute vapourization interference effects in a direct current plasma. Anal. Chem. 51(14): 2403-2405.

Johnson, N.M. 1979. Acid rain: Neutralization within the Hubbard Brook ecosystem and regional implications. Science 204: 497-499.

Johnson, N.M., Driscoll, C.T., Eaton, J.S., Likens, G.E. and McDowell, W.H. 1981. "Acid rain", dissolved aluminum and chemical weathering at the Hubbard Brook Experimental Forest, New Hampshire, U.S.A. Geochim. Cosmochim. Acta 45(9): 1421-1438.

Jones, J.P. and Fox, R.L. 1978. Phosphorus nutrition of plants influenced by manganese and aluminum uptake from an oxisol. Soil Sci. 126: 230-236.

Jones, J.R.E. 1939. The relation between the electrolytic solution pressures of the metals and their toxicity to the stickleback (Gasterosteus aculeatus L.). J. Exp. Biol. 16: 425-437.

Jones, J.R.E. 1964. Fish and river pollution. Butterworths, London. p. 66.

Jones, L.H. 1961. Aluminum uptake and toxicity in plants. Plant Soil 13: 292-310.

Jordan, J.W. 1961. Pulmonary fibrosis in a worker using an aluminum power. Br. J. Ind. Med. 18: 21.

Joseph, J.M. 1953. Microbiological study of acid mine waters: Preliminary report. Ohio J. Sci. 53: 123-127.

Julshamn, K., Anderson, K.-J., Willassen, Y. and Braekkan, O.R. 1978. A routine method for the determination of aluminum in human tissue samples using standard addition and graphite furnace atomic absorption spectrophotometry. Anal. Biochem. 88: 552-559.

Kaehny, W.D., Alfrey, A.C., Holman, R.E. and Shorr, W.J. 1977a. Aluminum transfer during hemodialysis. Kidney Int. 12: 361-365.

Kaehny, W.D., Hegg, A.P. and Alfrey, A.C. 1977b. Gastrointestinal absorption of aluminum from aluminum containing antacids. New Engl. J. Med. 296: 1389-1391.

Kamburov, J. 1980. Screening of pasture legumes for tolerance to aluminum. In Proc. 9th Natl. Congr., Soil Sci. Soc. South Africa. Tech. Commun. No. 174, Dep. Agric. Fish. Durban, South Africa. pp. 82-90.

Kamprath, E.J. 1970. Exchangeable aluminum as a criterion for liming leached mineral soils. Soil Sci. Soc. Am. Proc. 34: 252-254.

Karlik, S.J. 1979. Aluminum interactions with DNA and other polynucleotides. Ph.D. Thesis, Univ. of Toronto, Toronto, Ontario.

Karlik, S.J., Eichhorn, G.L. and McLachlan, D.R.C. 1980. Molecular interactions of aluminum with DNA. Neurotoxicology 1(4): 83-88.

Kato, T. 1973. Toxicity of chemical substances (heavy metals, etc.) to fish and animals. Nagoya Shiritsu Daigaku Igakkai Zasshi 24: 11.

Katz, A.M. 1970. Contractile proteins of the heart. Physiol. Rev. 50(1): 63-158.

Kehoe, R.A., Cholak, J. and Storey, R.V. 1940. Spectrochemical study of the normal ranges of concentration of certain trace metals in biological materials. J. Nutr. 19: 579-592.

Keller, W. and Conroy, N. 1981. Planktonic crustacea in lakes of the Greater Sudbury Area. Ontario Ministry of the Environment, Toronto, Ontario.

Kenttamaa, J. 1955. The hydrolysis of aluminum chloride. Acad. Sci. Fenn. Ann. Ser. A. Sect. II. No. 67.

Kerr, D.N.S. 1981. Renal osteomalacia. In Proc. 8th Int. Congr. Nephrol. Edited by W. Zurukzoglu, M. Papadimitrious, M. Pyrpasopoulos, M. Sion and C. Zamboulis. Bassle: Krager. pp. 221-228.

Kerridge, P.C. and Kronstad, W.K. 1968. Evidence of genetic resistance to aluminum toxicity in wheat (*Triticum aestivum* VIII., Host). Agron. J. 60: 710-712.

Kerridge, P.C., Dawson, M.D. and Moore, D.P. 1971. Separation of degrees of aluminum tolerance in wheat. Agron. J. 63: 586-691.

Keyser, H.H. and D.N. Munns. 1979. Effects of calcium, manganese, and aluminum on growth of rhizobia in acid media. Soil Sci. Soc. Am. J. 43: 500-503.

King, D.L., Simmler, J.J., Decker, C.S. and Ogg, C.W. 1974. Acid strip mine lake recovery. J. Water Pollut. Control Fed. 46: 2301-2315.

King, S.W., Wils, M.R. and Savory, J. 1979. Serum binding of aluminum. Res. Commun. Chem. Pathol. Pharmacol. 26: 161-169.

Kirsner, J.B. 1943. Effect of calcium carbonate, aluminum phosphate and aluminum hydroxide on mineral excretion in man. J. Clin. Invest. 22: 47-52.

Kittrick, J.A. 1966. The free energy of formation of gibbsite and $Al(OH)_4^-$ from solubility measurements. Soil Sci. Soc. Am. Proc. 30: 597-598.

Klein, G.L., Targoff, C.M., Ament, M.E., Sherrard, D.J., Bluestone, R., Young, J.H., Norman, A.W. and Coburn, J.W. 1980. Bone disease associated with total parenteral nutrition. Lancet 2: 1041-1044.

Ko, W.H. and Hora, F.K. 1972. Identification of an Al ion as a soil fungitoxin. Soil Sci. 113: 42.

Koirtyohann, S.R., Glass, E.D. and Lichte, F.E. 1981. Some observations on perchloric acid interferences in furnace atomic absorption. Appl. Spectrosc. 35(1): 22-26.

Koizumi, H., Yasuda, K. and Katsyama, M. 1977. Atomic absorption spectrophotometry based on the polarization characteristics of the Zeeman effect. Anal. Chem. 49(8): 1106-1112.

Kopp, J.F. and Kroner, R.C. 1970. Trace metals in waters of the United States. Federal Water Pollution Control Administration, Cincinnati, Ohio.

Korenaga, T., Motomizu, S. and Toli, K. 1980. Extraction - photometric determination of aluminum in river water with pyrocatechol violet and a quaternary ammonium salt. Talanta 27: 33-38.

Koryak, M., Shapiro, M.A. and Sykora, J.L. 1972. Riffle zoobenthos in streams receiving acid mine drainage. Water Res. 6: 1239-1247.

Kovalchik, M.T., Kaehny, W.D., Hegg, A.P., Jackson, F.T. and Alfrey, A.C. 1978. Aluminum kinetics during hemodialysis. J. Lab. Clin. Med. 92(5): 712-720.

Kramer, J. 1981. Aluminum: Chemistry, analysis and biology. Unpublished manuscript. Dep. of Geology, McMaster Univ., Hamilton, Ontario.

Kramer, J.R. and Hummel, J. 1985. Acute effect of aluminum to shiner minnows. Poster presentation, Int. Symp. Acidic Precipitation, Sept. 15-20, Muskoka, Ontario.

Kramer, J.R., Gleed, J., Johansson, R., Speakman, K. and Playle, R. 1981. Aluminum: chemistry, analysis and biology. Environ. Geochem. Rep. No. 81/2. Dep. of Geology, McMaster Univ., Hamilton, Ontario. 174 pp.

Krantzberg, G. 1985. Metal concentrations in benthic insect larvae and emergent adults as a function of sediment contamination. In Proc. Int. Conf. on Heavy Metals in the Environment, Athens, Greece. Vol. 2. CEP Consultants. pp. 159-161.

Kraut, J.A., Shinaberger, J.H., Singer, F.R., Sherrard, D.J., Saxton, J., Miller, J.H., Kurokawa, K. and Coburn, J.W. 1983. Parathyroid gland responsiveness to acute hypocalcemia in dialysis osteomalacia. Kidney Int. 23: 725-730.

Krishnan, S.S., Quittkat, S. and Crapper, D.R. 1976. Atomic absorption analysis for traces of aluminum and vanadium in biological tissue. A critical evaluation of the graphite furnace analyser. Can. J. Spectrosc. 21(1): 25-30.

Krug, E.C. and Isaacson, P.J. 1984. Comparison of water and dilute acid treatment on organic and inorganic chemistry of leachate from organic-rich horizons of an acid forest soil. Soil Sci. 137: 370-378.

Kruidhof, H. 1978. The determination of small amounts of aluminum and silicon in stabilized zirconia ceramics. Anal. Chim. Acta 99: 193-195.

Kubota, H. 1956. Properties and volumetric determination of aluminum. Diss. Abstr. 16: 84.

Kwiatkowski, R.E. and Roff, J.C. 1976. Effects of acidity on the phytoplankton and primary productivity of selected northern Ontario lakes. Can. J. Bot. 54: 2546-2561.

Lackey, J.B. 1938. The flora and fauna of surface waters polluted by acid mine drainage. Public Health Rep. 53: 1499-1507.

LaCroix, S. 1949. Etude de quelques complexes et composes peu solubles des ions Al^{3+}, Ga^{3+}, In^{3+}. Ann. Chim. 4: 5-83.

Lafever, H.N., Campbell, L.G. and Foy, C.D. 1977. Differential response of wheat cultivars to aluminum. Agron. J. 69: 563-568.

Lai, J.C.K., Guest, J.F., Lim, L. and Davison, A.N. 1978. Biochem. Soc. Trans. 14: 253.

Lai, J.C.K., Guest, J.F., Leung, T.K.C., Lim, L. and Davison, A.N. 1980. The effects of cadmium, manganese and aluminum on sodium-potassium-activated and magnesium-activated adenosine triphosphatase activity and choline uptake in rat brain synaptosomes. Biochem. Pharmacol. 29: 141-146.

Lancaster, L.A. and Balasubramanian, R. 1974. An automated procedure for the determination of aluminum in soil and plant digests. J. Sci. Food Agric. 25: 381-386.

Langmyhr, F.J. and Tsalev, D.L. 1977. Atomic absorption spectrometric determination of aluminum in whole blood. Anal. Chim. Acta 92: 79-83.

Lapresle, J., Duckett, S., Galle, P. and Cartier, L. 1975. Documents cliniques anatomiques et biophysiques dans un encephalopathie avec presence de depots d'aluminium. C.R. Soc. Biol. 169: 282-285.

LaZerte, B.D. 1984. Forms of aqueous aluminum in acidified catchments of central Ontario: a methodological analysis. Can. J. Fish. Aquat. Sci. 41(5): 766-776.

LaZerte, B.D. and Playle, R. 1984. A comparison of methods for the speciation of aluminum in freshwaters. Unpublished manuscript. Dorset Research Centre, Ontario Ministry of the Environment, Dorset, Ontario, and Dep. of Geology, McMaster Univ., Hamilton, Ontario.

Lee, C. and Harvey, H.H. 1985. Localization of aluminum in fish tissue. Poster presentation, Int. Symp. Acidic Precipitation, Sept. 15-20, Muskoka, Ontario.

Lee, C.R. 1971a. Influence of aluminum on plant growth and tuber yield of potatoes. Agron. J. 63: 363-364.

Lee, C.R. 1971b. Influence of aluminum on plant growth and mineral nutrition of potatoes. Agron. J. 63: 604-608.

Lee, E.H., Heggestad, H.E. and Bennett, J.H. 1982. Effects of sulfur dioxide fumigation in open-top field chambers on soil acidification and exchangeable aluminum. J. Environ. Qual. 11: 99-102.

Leivestad, H. 1985. Toxic effects of aluminum on eggs and larvae of the Atlantic salmon (S. salar). Poster presentation, Int. Symp. Acidic Precipitation, Sept. 15-20, Muskoka, Ontario.

Leung, F.Y. and Henderson, A.R. 1982. Improved determination of aluminum in serum and urine with use of a stabilized temperature platform furnace. Clin. Chem. 28: 2139-2143.

Leppard, G.G. 1985. Effects of acid stress on bacterial responses to toxic metals in aquatic ecosystems. Poster presentation, Int. Symp. Acidic Precipitation, Sept. 15-20, Muskoka, Ontario.

Leta, D.P. and Morrison, G.H. 1980. Ion implantation for in-situ quantitative ion microprobe analysis. Anal. Chem. 52: 277-280.

Lichte, F.E., Hopper, S. and Osborn, T.W. 1980. Determination of silicon and aluminum in biological matrices by inductively coupled plasma emission spectrometry. Anal. Chem. 52: 120-124.

Lieberherr, M., Grosse, B., Cournot-Witmer, G., Thil, C.L. and Balsan, S. 1982. In vitro effects of aluminum on bone phosphatases: a possible interaction with PTH and vitamin D3 metabolites. Calcif. Tissue Res. 34: 280-284.

Likens, G.E. and Bormann, F.H. 1972. Nutrient cycling in ecosystems. In Ecosystem structure and function. Proc. 31st Annu. Biol. Colloq. Edited by J.D. Wiens. Oregon State Univ. Press, Corvallis, Oregon.

Likens, G.E., Bormann, F.H., Pierce, R.S., Eaton, J.S. and Johnson, N.M. 1977. Biogeochemistry of a forested ecosystem. Springer-Verlag, New York.

Linton, R.W., Williams, P., Evans, C.A. and Natusch, D.F.S. 1977. Determination of the surface predominance of toxic elements in airborne particles by ion microprobe mass spectrometry and auger electron spectrometry. Anal. Chem. 49(11): 1514-1521.

Linzon, S.N. 1985. Personal communication. Ontario Ministry of the Environment, Toronto, Ontario.

Lione, A. 1983. The prophylactic reduction of aluminum intake. Food Chem. Toxicol. 21(1): 103-109.

Lione, A. and Smith, J.C. 1982. The mobilization of aluminum from three brands of chewing gum. Food Chem. Toxicol. 20: 945-946.

Lipstein, B. and Hurwitz, S. 1982. The effect of aluminum on the phosphorus availability in algae-containing diets. Poult. Sci. 61: 951-954.

Litman, A. 1967. Reactive and nonreactive aluminum hydroxide gels: dose-response relationships *in vivo*. Gastroenterology 52: 948-951.

Long, J.F., Nagode, L.A., Kindig, O. and Liss, L. 1980. Axonal swellings of purkinje cells in chickens associated with high intake of 1,25-$(OH)_2D_3$ and elevated dietary aluminum including X-ray microanalysis. Neurotoxicology 1: 111-120.

Lopes, A.S. and Cox, F.R. 1977. A survey of the fertility status of surface soils under "cerrado" vegetation in Brasil. Soil Sci. Soc. Am. J. 41: 742-746.

Lotz, M., Zisman, E. and Bartter, F.C. 1968. Evidence for a phosphorus-depletion syndrome in man. N. Engl. J. Med. 278: 409-415.

Luciuk, G.M. and Huang, P.M. 1974. Effect of monosilicic acid on hydrolytic reactions of aluminum. Soil Sci. Soc. Am. Proc. 38(2): 235-244.

Lund, Z.F. 1970. The effect of calcium and its relation to some other cations on soybean growth. Soil Sci. Soc. Am. Proc. 34: 456-459.

Lunt, H.A. 1932. Profile characteristics of New England forest soils. Conn. Agric. Exp. Stn. New Haven Bull. 342.

Lynn, R. and Brock, T.D. 1969. Notes on the ecology of a species of *Zygogonium* (Kutz) in Yellowstone National Park. J. Phycol. 5: 181-185.

MacDonald, D.D., Butler, P. and Owen, D. 1973. Hydrothermal hydrolysis of Al^{3+} and the precipitation of boehmite from aqueous solution. J. Phys. Chem. 77(20): 2474-2479.

MacLeod, L.B. and Jackson, L.P. 1965. Effect of concentration of the Al ion on root development and establishment of legume seedlings. Can. J. Soil Sci. 45: 221-234.

Magistad, O.C. 1925. The aluminum content of the soil solution and its relation to soil reaction and plant growth. Soil Sci. 20: 181-213.

Malavolta, E., Nogueira, F.D., Oliveira, I.P., Nakayama, L. and Eimori, I. 1981. Aluminum tolerance in sorghum and bean - methods and results. J. Plant Nutr. 3: 1-4.

Malcolm, R.L. and McCracken, R.J. 1968. Canopy drip - a source of mobile soil organic matter for mobilization of iron and aluminum. Soil Sci. Soc. Am. J. 32: 834.

Malley, D.F. 1980. Decreased survival and calcium uptake by the crayfish _Orconectes virilis_ in low pH. Can. J. Fish. Aquat. Sci. 37: 364-372.

Malley, D.F. and Chang, P.S.S. 1985. Effects of aluminum and acid on calcium uptake by the crayfish _Orconectes virilis_. Arch. Environ. Contam. Toxicol. 14: 739-748.

Manahan, S.E. 1975. The nature and composition of natural waters. _In_ Environmental chemistry. 2nd ed. Willard Grant Press, Boston.

Mansour, J.M., Ehrlich, A. and Mansour, T.E. 1983. Dual effects of aluminum as activator and inhibitor of adenylate cyclase in the liver fluke _Fasciola hepatica_. Biochem. Biophys. Res. Commun. 112(3): 911-918.

Marion, G.M., Hendricks, D.M., Dutt, G.R. and Fuller, W.H. 1976. Aluminum and silica solubility in soils. Soil Sci. 121: 76-85.

Marquis, J.K. 1983. Aluminum inhibition of human serum cholinesterase. Bull. Environ. Contam. Toxicol. 31(2): 164-169.

Marquis, J.K. and Lerrick, A.J. 1982. Noncompetitive inhibition by aluminum and yttrium of acetylcholinesterase from _Electrophorus electricus_. Biochem. Pharmacol. 31(7): 1437-1440.

Martin, J.H. and Knauer, G.A. 1973. The elemental composition of plankton. Geochim. Cosmochim. Acta 37: 1639-1653.

Mathews, A.P. 1904. The relation between solution tension, atomic volume, and the physiological action of the elements. Am. J. Physiol. 10: 290.

Matijevic, E. and Tezak, B. 1953. Detection of polynuclear complex Al ions by means of coagulation measurements. J. Phys. Chem. 57: 951-954.

Matijevic, E., Mathai, K.A., Otterwill, R.H. and Kerker, M. 1961. Detection of metal ion hydrolysis by coagulation. III. Aluminum. J. Phys. Chem. 65: 826-830.

Mathan, K.K. 1980. Effect of various levels of aluminum on the dry matter yield, content and uptake of phosphorus, aluminum, manganese, magnesium, and iron in maize. Madras Agric. J. 11: 751-757.

Matsumoto, H. and Mormura, S. 1980. Repressed template activity of chromatin of pea roots treated by aluminum. Plant Cell Physiol. 21: 951-959.

Matsumoto, H., Hirasawa, E. and Takahashi, E. 1976a. Localization of aluminum in tea leaves. Plant Cell Physiol. 17: 627-631.

Matsumoto, H., Hirasawa, E., Morimura, S. and Takahashi, E. 1976b. Localization of aluminum in tea leaves. Plant Cell Physiol. 17: 890-895.

Matsumoto, H., Hirasawa, E., Torikai, H. and Takahashi, E. 1976c. Localization of absorbed aluminum in pea root and its binding to nucleic acids. Plant Cell Physiol. 17: 127-137.

Matsusaki, K., Yoshino, T. and Yamamoto, Y. 1979. A method for removal of chloride interference in determination of aluminum by atomic-absorption spectrometry with a graphite furnace. Talanta 26: 377-380.

May, H.M., Helmke, P.A. and Jackson, M.L. 1979a. Determination of mononuclear dissolved aluminum in near-neutral waters. Chem. Geol. 24: 259-269.

May, H.M., Helmke, P.A. and Jackson, M.L. 1979b. Gibbsite solubility and thermodynamic properties of hydroxy-aluminum ions in aqueous solution at 25°C. Geochim. Cosmochim. Acta 43: 861-868.

Mayer, R. 1983. Interaction of forest canopies with atmospheric constituents: aluminum and heavy metals. In Effects of accumulation of air pollutants in forest ecosystems. Edited by B. Ulrich and J. Pankrath. D. Reidel Publ. Co., Boston. pp. 47-55.

Mayor, G.H., Keiser, J.A., Makdani, D. and Ku, P.K. 1977. Aluminum absorption and distribution: effect of parathyroid hormone. Science 197: 1187-1189.

Mayor, G.H., Sprague, S.M., Hourani, M.R. and Sanchez, T.V. 1980. Parathyroid hormone-mediated aluminum deposition and egress in the rat. Kidney Int. 17: 40-44.

McCormick, L.H. and Steiner, K.C. 1978. Variation in aluminum tolerance among six genera of trees. For. Sci. 24: 565-568.

McDermott, J.R., Smith, A.I.K., Igbal, K. and Wisniewski, H.M. 1977. Aluminum and Alzheimer's disease. Lancet 2: 710-711.

McGuigan, H.A. 1927. The pharmacology of iron and aluminum in relation to therapeutic uses. J. Lab. Clin. Med. 12: 790.

McLaughlin, A.I.G., Kazontzis, G., King, E., Teare, D., Porter, R.J. and Owen, R. 1962. Pulmonary fibrosis and encephalopathy associated with the inhalation of aluminum dust. Br. J. Ind. Med. 19: 253.

McLean, F.T. and Gilbert, B.E. 1927. The relative aluminum tolerance of crop plants. Crop Sci. 24: 163-175.

McLean, F.T. and Gilbert, B.E. 1928. Aluminum toxicity. Plant Physiol. 3: 293-302.

McQuaker, N.R., Kluckner, P.D. and Chang, G.N. 1979. Calibration of an inductively coupled plasma - atomic emission spectrometer for the analysis of environmental materials. Anal. Chem. 51(7): 888-895.

Medappa, K.C. and Dana, M.N. 1970. Tolerance of cranberry plants to manganese, iron, and aluminum. J. Am. Soc. Hortic. Sci. 95: 107-110.

Meinck, F., Stoof, H. and Kohlschütter, H. 1968. Industrie-Abwässer, Gustav Fischer Verlag, Stuttgart. p. 635.

Memon, A.R., Chino, M. and Yatazawa, M. 1981. Microdistribution of aluminum and manganese in the tea leaf tissues as revealed by X-ray microanalyzer. Commun. Soil Sci. Plant Anal. 12: 441-452.

Meredith, P.A., Elliott, H.L., Campbell, B.C. and Moore, M.R. 1979. Changes in serum aluminum, blood zinc, blood lead, and erythrocyte deltaaminolevulinic acid dehydratase activity during hemodialysis. Toxicol. Lett. 4(15): 419-424.

Merryfield, R.N. and Lloyd, R.C. 1979. Simultaneous determination of metals in oil by inductively coupled plasma emission spectrometry. Anal. Chem. 51(12): 1965-1968.

Mesdag, J. and Slootmaker, L.A. 1969. Classifying wheat varieties for tolerance to high soil acidity. Soil Sci. 10: 153-217.

Mesmer, R.E. and Baes, C.F. 1971. Acidity measurements at elevated temperatures. V. Aluminum ion hydrolysis. Inorg. Chem. 10: 2290.

Miller, C.A. and Levine, E.M. 1974. Effects of aluminum salts on cultured neuroblastoma cells. J. Neurochem. 22: 751-758.

Miller, G.E., Wile, I. and Hitchin, G.G. 1983. Patterns of accumulation of selected metals in members of the soft-water macrophyte flora of central Ontario, Canada, lakes. Aquat. Bot. 15(1): 53-64.

Ministry of the Environment. 1982a. Sudbury Environmental Study. Studies of lakes and watersheds near Sudbury, Ontario: final limnological report. Ontario Ministry of the Environment Doc. SES009/82, Rexdale, Ontario.

Ministry of the Environment. 1982b. Sudbury Environmental Study. Studies of lakes and watersheds near Sudbury, Ontario: final limnological report. Supplement. Ontario Ministry of the Environment Doc. SES009/82, Rexdale, Ontario.

Minkina, A.L. 1946. On the action of iron and aluminum on fish. Trudy Mosk. Zooparka 3: 23.

Mirasol, J.J. 1921. Aluminum as a factor in soil acidity. Soil Sci. 10: 153-217.

Misra, U.K., Blancher, R.W. and Upchurch, W.J. 1974. Aluminum content of soil extracts as a function of pH and ionic strength. Soil Sci. Soc. Am. Proc. 38: 897-902.

Mitchell, J. 1959. Pulmonary fibrosis in an aluminum worker. Br. J. Ind. Med. 16: 123.

Mitchell, J., Manning, G.B., Molyneux, M. and Lane, R.E. 1961. Pulmonary fibrosis in workers exposed to finely powdered aluminium. Br. J. Ind. Med. 18: 10.

Molan, B. 1980. The analysis of atmospheric precipitation in Czechoslovakia. In Proc. Int. Conf. Ecological Impact Acid Precipitation, Norway. Edited by D. Drablos and A. Tollan. SNSF Project. pp. 124-125.

Mollitor, A.V. and Raynal, D.J. 1982. Acid precipitation and ionic movement in Adirondack forest soils. Soil Sci. Soc. Am. J. 46: 137-141.

Moody, J.R. and Lindstrom, R.M. 1977. Selection and cleaning of plastic containers for storage of trace element samples. Anal. Chem. 49(14): 2264-2267.

Moore, D.P. 1974. Physiological effects of pH on roots. In The plant root and its environment. Edited by E.W. Carson. Univ. of Virginia Press, Charlottesville, Virginia. pp. 135-151.

Morrill, L.G., Mahilum, B.C. and Mohiuddin, S.H. (Editors.) 1982. Organic compounds in soils: sorption, degradation and persistence. Ann Arbor Sci., Ann Arbor, Michigan. 326 pp.

Morrissey, J., Rothstein, M., Mayor, G. and Slatopolsky, E. 1983. Suppression of parathyroid hormone secretion by aluminum. Kidney Int. 23(4): 699-704.

Mugwira, L.M. 1980. Growth and Ca, Mg, K and P uptake by triticale, wheat and rye at four Al levels. J. Plant Nutr. 2: 591-606.

Mugwira, L.M. and Elgawhary, S.M. 1979. Aluminum accumulation and tolerance of triticale and wheat in relation to root cation exchange capacity. Soil Sci. Soc. Am. J. 43: 736-740.

Mugwira, L.M., Patel, S.V. and Fleming, A.L. 1980. Aluminum effects on growth and Al, Ca, Mg, K, and P levels in triticale, wheat, and rye. Plant Soil 57: 467-470.

Mugwira, L.M., Sapra, V.T., Patel, S.V. and Choudrey, M.A. 1981. Aluminum tolerance of triticale and wheat cultivars developed in different regions. Agron. J. 73: 470-475.

Mullette, K.J. 1975. Stimulation of growth in Eucalyptus due to aluminum. Plant Soil 42: 495-499.

Muniz, I.P. and Leivestad, H. 1980a. Acidification - effects on freshwater fish. In Proc. Int. Conf. Ecological Impact Acid Precipitation, Norway. Edited by D. Drablos and A. Tollan. SNSF Project. pp. 84-92.

Muniz, I.P. and Leivestad, H. 1980b. Toxic effects of aluminum on the brown trout, Salmo trutta L. In Proc. Int. Conf. Ecological Impact Acid Precipitation, Norway. Edited by D. Drablos and A. Tollan. SNSF Project. pp. 320-321.

Munns, D.N. 1965. Soil acidity and growth of a legume. Aust. J. Agric. Res. 16: 733-766.

Munns, D.N., Keyser, H.H., Fogle, V.W., Hohenberg, J.S., Righetti, T.L., Louter, D.S., Zaroug, M.G., Clarkin, K.L. and Whitacre, K.W. 1979. Tolerance of soil acidity in symbioses of mung bean with rhizobia. Agron. J. 71: 256-260.

Murdoch, H.R. 1953. Some data on toxicity of metals in wastes to fish life are presented. Ind. Eng. Chem. 49: 99A.

Murray, J.J. and Foy, C.D. 1978. Differential tolerances of turfgrass cultivars to an acid soil high in exchangeable aluminum. Agron. J. 70: 769-774.

Mushak, P. 1977. GLC of metal ions via chelation and non-chelation. In Handbook of derivatives for chromatography. Edited by K. Blau and G.S. King. Heyden Press, London. pp. 440-444.

Nadkarni, R.A. 1980. Multitechnique multielemental analysis of coal and fly ash. Anal. Chem. 52: 929-935.

Naidoo, G., Stewart, J.M. and Lewis, J.R. 1978. Accumulation sites of aluminum in snapbean and cotton roots. Agron. J. 70(3): 489-492.

Nair, V.D. and Prenzel, J. 1978. Calculations of the equilibrium concentration of mono- and polynuclear hydroxyaluminum species at different pH and total aluminum concentrations. Z. Pflanzenernaehr. Bodenkd. 141(6): 741-751.

Nalewajko, C. and Paul, B. 1985. Effects of manipulations of aluminum concentrations and pH on phosphate uptake and photosynthesis of planktonic communities in two Precambrian Shield lakes. Unpublished manuscript. Dep. of Botany, Univ. of Toronto, Toronto, Ontario.

Nazarenko, V.A. and Biryuk, E.A. 1974. The hydrolysis constant of aluminum ions in solutions with variable ionic strength: the correlation of such constants for group III ions with the position of the element in the periodic system. Russ. J. Inorg. Chem. 19(3): 341-343.

Nazarenko, V.A. and Nevskaya, E.M. 1969. Spectrophotometric determination of the constants of mononuclear hydrolysis of aluminum ions. Russ. J. Inorg. Chem. 14: 1696-1699.

Negoro, K. 1939. A Pinnularia from Okama, an acidotrophic crater lake of volcano Zaô. Jpn. J. Limnol. Tokyo 9: 176-179.

Nelson, L.E. 1983. Tolerances of 20 rice varieties to excess Al and Mn. Agron. J. 75: 134-138.

Neville, C.M. 1985. Studies on the mechanism of toxicity of acid and aluminum to juvenile rainbow trout in a low ion environment. Poster presentation, Int. Symp. Acidic Precipitation, Sept. 15-20, Muskoka, Ontario.

Ng Kee Kwong, K.F. and Huang, P.M. 1977. Influence of citric acid on the hydrolytic reactions of aluminum. Soil Sci. Soc. Am. J. 41: 692-697.

Ng Kee Kwong, K.F. and Huang, P.M. 1978. Sorption of phosphate by hydrolytic reaction products of aluminum. Nature (London) 271(5643): 336-338.

Nieboer, E. and Richardson, D.H.S. 1980. The replacement of the nondescript term "heavy metals" by a biologically and chemically significant classification of metal ions. Environ. Pollut. Ser. B 1: 3-26.

Nilssen, J.P. 1980. Acidification of a small watershed in southern Norway and some characteristics of acidic aquatic environments. Int. Rev. Gesamten Hydrobiol. 65: 177-207.

Nilsson, S.I. and Bergkvist, B. 1983. Aluminum chemistry and acidification processes in a shallow podzol on the Swedish west coast. Water Air Soil Pollut. 20(3): 311-329.

Nilsson, S.I., Wiklander, G. and Farrell, E.P. 1983. Stores of exchangeable base cations and aluminum in lysimeters previously treated with sulphuric acid or NPK with and without irrigation. For. Ecol. Manage. 5: 87-108.

Nordstrom, D.K. 1982. The effect of sulfate on aluminum concentrations in natural waters. Some stability relations in the system $Al_2O_3 \cdot SO_3 \cdot H_2O$ at 298K. Geochim. Cosmochim. Acta 46(4): 681-692.

Norton, S.A., Hanson, D.W. and Campana, R.J. 1980. The impact of acidic precipitation and heavy metals on soils in relation to forest ecosystems. Presented at the Int. Symp. on Effects of Air Pollutants on Mediterranean and Temperate Forest Ecosystems, June 22-27, Riverside, California.

Nygaard, D.D. and Gilbert, T.R. 1981. Emission line enhancement in a dc plasma. Appl. Spectrosc. 35: 52-56.

Nyholm, N.E. 1981. Evidence of involvement of aluminum in causation of defective formation of eggshells and of impaired breeding in wild passerine birds. Environ. Res. 26: 363-371.

Ogner, G. and Teigen, O. 1980. Effects of acid irrigation and liming on two clones of Norway spruce. Plant Soil 57: 305-321.

O'Hare, J.A. and Murnaghan, D.J. 1982. Reversal of aluminum induced hemodialysis anemia by a low-aluminum dialysate. New Engl. J. Med. 306: 654-656.

Öhman, L.-O. and Försling, W. 1981. Equilibrium and structural studies of silicon (IV) and aluminum (III) in aqueous solution. 3. A potentiometric study of aluminum (III) hydrolysis and aluminum (III) hydroxo carbonates in 0.6 M Na(Cl). Acta Chem. Scand. A 35: 795-802.

Öhman, L.-O. and Sjöberg, S. 1981. Equilibrium and structural studies of silicon (IV) and aluminum (III) in aqueous solution. 1. The formation of ternary mononuclear and polynuclear complexes in the system Al^{3+} - gallic acid - OH$^-$. A potentiometric study in 0.6 M Na(Cl). Acta Chem. Scand. A 35: 201-212.

Öhman, L.-O. and Sjöberg, S. 1982. Equilibrium and structural studies of silicon (IV) and aluminum (III) in aqueous solution. 4. A potentiometric study of polynuclear aluminum (III) hydroxo complexes with gallic acid in hydrolyzed aluminum (III) solutions. Acta Chem. Scand. A 36: 47-53.

Öhman, L.-O. and Sjöberg, S. 1983a. Equilibrium and structural studies of silicon (IV) and aluminum (III) in aqueous solution. 9. A potentiometric study of mono- and poly-nuclear aluminum (III) citrates. J. Chem. Soc. Dalton Trans. 1983: 2513-2517.

Öhman, L.-O. and Sjöberg, S. 1983b. Equilibrium and structural studies of silicon (IV) and aluminum (III) in aqueous solution. 10. A potentiometric study of aluminum (III) pyrocatecholates and aluminum (III) hydroxo pyrocatecholates in 0.6 M Na(Cl). Polyhedron 2(12): 1329-1335.

Öhman, L.-O. and Sjöberg, S. 1983c. Equilibrium and structural studies of silicon (IV) and aluminum (III) in aqueous solution. 8. A potentiometric study of aluminum (III) salicylates and aluminum (III) hydroxy salicylates in 0.6 M Na(Cl). Acta Chem. Scand. A 37: 875-880.

Öhman, L.-O., Sjöberg, S. and Ingri, N. 1983. Equilibrium and structural studies of silicon (IV) and aluminum (III) in aqueous solution. 7. Redox, hydrolysis and complexation equilibria in the system Al^{3+} - 1,2-naphthoquinone-4-sulfonate/1,2-dihydroxy-naphthalene-4-sulfonate-OH$^-$. A potentiometric study in 0.6 M Na(Cl). Acta Chem. Scand. A 37: 561-568.

Ohtawa, M., Seko, M. and Takayama, F. 1983. Effect of aluminum on lipid peroxidation in rats. Chem. Pharm. Bull. 31: 1415-1418.

Oka, Y. 1938. The fundamental reactions in analytical chemistry. I. Reactions of caustic soda with metallic ions. J. Chem. Soc. Jpn. 59: 971-1013.

Ondreicka, R., Kortus, J. and Ginter, E. 1971. Aluminum, its absorption, distribution, and effects on phosphorus metabolism. In Intestinal absorption of metal ions, trace elements and radionuclides. Edited by S.C. Skoryna and D. Waldron-Edward. Pergamon Press, New York. pp. 293-305.

Ormerod, S.J., Allinson, N., Hudson, D. and Tyler, S.J. 1986. The distribution of breeding Dippers (Cinclus cinclus; Aves) in relation to stream acidity in upland Wales. J. Freshwater Biol. (In press.)

Oshima, S. 1931. On the toxic action of dissolved salts and their ions upon young eels (Anguilla japonica). J. Imp. Fish. Exp. Stn. 2: 139.

Otchere-Boateng, J. and Ballard, T.M. 1981. Effect of urea fertilization on leaching of micronutrient metals and aluminum from forest soil columns. Can. J. For. Res. 11: 763-767.

Ott, S.M., Maloney, N.A., Klein, G.L., Alfrey, A.C., Ament, M.E., Coburn, J.W. and Sherrard, D.J. 1983. Aluminum is associated with low bone formation in patients receiving chronic parenteral nutrition. Ann. Intern. Med. 98: 910-914.

Ottaway, J.M., Bezur, L. and Marshall, J. 1980. An echelle monochromator system for the measurement of sensitive carbon furnace atomic emission signals. Analyst 105: 1130-1133.

Pajos, T. 1984. Personal communication. Institute for Environmental Studies, Univ. of Toronto, Toronto, Ontario.

Parkinson, I.S., Ward, M.K., Feest, T.G., Fawcett, R.W.P. and Ker, D.N.S. 1979. Fracturing dialysis osteodystrophy and dialysis encephalopathy: an epidemiological survey. Lancet 1: 406-409.

Parks, G.A. 1972. Free energies of formation and aqueous solubilities of aluminum hydroxides and oxihydroxides at 25°C. Am. Mineral. 57: 1163-1189.

Parsons, J.D. 1968. The effect of acid strip mine effluent on the ecology of a stream. Arch. Hydrobiol. 65: 25-50.

Parsons, V., Davies, C., Goode, C., Ogg, C. and Siddiqui, J. 1971. Aluminum in bone from patients with renal failure. Br. Med. J. 4: 273-275.

Patockna, J. 1971. The influence of Al^{3+} on cholinesterase and acetylcholinesterase activity. Acta Biol. Med. Germ. 26: 845-846.

Patterson, J.H. and Tyree, S.Y., Jr. 1973. A light-scattering study of the hydrolytic polymerization of aluminum. J. Colloid Interface Sci. 43(2): 389-397.

Paul, B.J. 1984. The effect of aluminum on phytoplankton. MSc Thesis, Univ. of Toronto, Toronto, Ontario. 196 pp.

Pavan, M.A. and Bingham, F.T. 1982. Toxicity of aluminum to coffee seedlings grown in nutrient solution. Soil Sci. Soc. Am. J. 46: 992-997.

Pavan, M.A., Bingham, F.T. and Pratt, P.F. 1982. Toxicity of aluminum to coffee in ultisols and oxisols amended with $CaCO_3$, $MgCO_3$, and $CaSO_4 \cdot 2H_2O$. Soil Sci. Soc. Am. J. 46: 1201-1207.

Pavan, M.A., Bingham, F.T. and Pratt, P.F. 1984. Redistribution of exchangeable calcium, magnesium, and aluminum following lime or gypsum applications to a Brasilian oxisol. Soil Sci. Soc. Am. J. 48: 33-38.

Pearson, R.W., Abruma, F. and Vincente-Chandler, J. 1962. Effect of lime and nitrogen applications on downward movement of calcium and magnesium in two tropical soils of Puerto Rico. Soil Sci. 93: 77-82.

Penny, C. and Adams, C. 1937. 4th Report, Royal Commission on Pollution of Rivers in Scotland. Vol. 2. Evidence. London. p. 377.

Perl, D.P. and Brody, A.R. 1979. Detection of focal accumulations of aluminum (Al) and silicon (Si) within neurofibrillary tangle bearing neurons of Alzheimer's disease. J. Neuropathol. Exp. Neurol. 38: 335. (Abstr. 102.)

Perl, D.P. and Brody, A.R. 1980. Alzheimer's disease: X-ray spectrometric evidence for aluminum accumulation in neurofibrillary tangle bearing neurons. Science 208: 297-299.

Perl, D.P., Gajdusek, D.C., Garruto, R.M., Yanagihara, R.T. and Gibbs, C.J., Jr. 1982. Intraneuronal aluminum accumulation in amyotrophic lateral sclerosis and Parkinsonism-dementia of Guam. Science 217: 1053-1055.

Persson, J.A., Frech, W. and Cedergren, A. 1977. Investigations of reactions involved in flameless atomic absorption procedures. V. An experimental study of factors affecting the determination of aluminum. Anal. Chim. Acta 92: 95-104.

Petit, T.L., Beiderman, G.B. and McMullen, P.A. 1980. Neurofibrillary degeneration, dendritic dying back and learning-memory deficits following aluminum administration: implications for brain aging. Exp. Neurol. 67: 152-162.

Pierre, W.H. and Stuart, A.D. 1933. Soluble aluminum studies: IV. The effects of phosphorus in reducing the detrimental effects of soil acidity on plant growth. Soil Sci. 36: 211-225.

Pierre, W.H., Pohlman, G.G. and McIlvaine, T.C. 1932. Soluble aluminum studies: I. The concentration of aluminum in the displaced soil solution of naturally acid soils. Soil Sci. 34: 145-160.

Pierre, W.H., Webb, J.R. and Shrader, W.D. 1971. Quantitative effects of nitrogen fertilizer on the development and downward movement of soil acidity in relation to level of fertilization and crop removal in a continuous corn cropping system. Agron. J. 63: 291-297.

Pionke, H.B. and Corey, R.B. 1967. Relations between acidic aluminum and soil pH, clay and organic matter. Soil Sci. Soc. Am. Proc. 31: 749-752.

Platts, M.M., Goode, G.C. and Hislop, J.S. 1977. Composition of the domestic water supply and the incidence of fractures and encephalopathy in patients on home dialysis. Br. Med. J. 2: 657-660.

Playle, R. 1983. Personal communication. Dep. of Geology, McMaster Univ., Hamilton, Ontario.

Playle, R., Gleed, J., Jonasson, R. and Kramer, J.R. 1982. Comparison of atomic absorption, spectrometric, spectrophotometric, and fluorimetric methods for determination of aluminum in water. Anal. Chim. 134: 369-376.

Polle, E., Konzak, C.F. and Kittrick, J.A. 1978. Visual detection of aluminum tolerance levels in wheat by hematoxylin staining in seedlings roots. Crop Sci. 18: 823-827.

Pratt, P.F. 1966. Aluminum. In Diagnostic criteria for plants and soils. Univ. of California, Div. of Agricultural Sciences, Riverside, California.

Price, W.J. 1972. Analytical atomic absorption spectrometry. Heyden and Sons Ltd., London, New York. p. 185.

Pulfer, K. 1981. Kinetik und Mechanismus der Aufloesung von γ-Al(OH)$_3$ in HNO$_3$-HF-Loesungen. Thesis, Univ. of Bern, Switzerland.

Pulley, T.E. 1950. The effect of aluminum chloride in small concentrations on various marine organisms. Texas J. Sci. 2: 405.

Que Hee, S.S. and Finelli, V.N. 1980. Colorimetric and flame AA analysis of aluminum in biological and aqueous media. Am. Chem. Soc. Pap. 180(1), Abstr. No. ANYL 121.

Ragland, J.L. and Coleman, M.T. 1960. The hydrolysis of aluminum salts in clay and soil systems. Soil Sci. Soc. Am. Proc. 24: 457-460.

Rally, C.E. 1983. The effect of aluminum and acidic conditions upon *Picea glauca* (Moench) Voss. Unpublished B.Sc. Thesis, Faculty of Forestry, Univ. of British Columbia, Vancouver, British Columbia.

Rasmussen, H.P. 1968. Entry and distribution of aluminum in *Zea mays*. Planta 81: 28-37.

Raupach, M. 1957. Investigations into the nature of soil pH. C.S.I.R.O. Aust. Soil Publ. No. 9.

Raupach, M. 1963. Solubility of simple aluminum compounds expected in soils. I. Hydroxides and oxi-hydroxides. Aust. J. Soil Res. 1: 28-62.

Rausch, W.V. and Bale, H.D. 1964. Small-angle X-ray scattering from hydrolyzed aluminum nitrate solutions. J. Chem. Phys. 40: 3391-3394.

Rawlence, D.J. and Whitton, J.S. 1977. Elements in aquatic macrophytes, water, plankton, and sediments surveyed in three north island lakes. N. Z. J. Mar. Freshwater Res. 11: 73-93.

Rees, W.J. and Sidrak, G.H. 1956. Plant nutrition on "fly ash". Plant Soil 8: 141-150.

Rees, W.J. and Sidrak, G.H. 1961. Inter-relationship of aluminum and manganese toxicities towards plants. Plant Soil 14: 101-117.

Reesman, A.L., Pickett, E.E. and Keller, W.D. 1969. Aluminum ions in aqueous solutions. Am. J. Sci. 267: 99-113.

Reid, D.A., Jones, G.D., Armiger, W.H., Foy, C.D., Koch, E.J. and Starling, T.M. 1969. Differential aluminum tolerance of winter barley varieties and selections in associated greenhouse and field experiments. Agron. J. 61: 218-222.

Reid, D.A., Fleming, A.L. and Foy, C.D. 1971. A method for determining aluminum response of barley in nutrient solution in comparison to response in Al-toxic soil. Agron. J. 63: 600-603.

Reis, B.F., Bergamin, H., Zagatto, E.A.G. and Krug, F.J. 1979. Merging zones in flow injection analysis. Part 3. Spectrophotometric determination of aluminium in plant and soil materials with sequential addition of pulsed reagents. Anal. Chim. Acta 107: 309-317.

Reuss, J.O. 1983. Implications of the calcium-aluminum exchange system for the effect of acid precipitation on soils. J. Environ. Qual. 12: 591-595.

Rhue, R.D., Grogan, C.O., Stockmeyer, E.W. and Everett, H.L. 1978. Genetic control of aluminum tolerance in corn. Crop Sci. 18: 1063-1067.

Richards, J.N. 1974. Studies of the phytoplankton and soil algae of two acid strip-mine impoundments in Tuscarawas County, Ohio. M.A. Thesis, Kent State Univ., Kent, Ohio. 56 pp. (Cited by Riley 1977.)

Richburg, J.S. and Adams, F. 1970. Solubility and hydrolysis of aluminum in soil solutions and saturated paste extracts. Soil Sci. Soc. Am. Proc. 34: 728-734.

Riley, C.V. 1977. Development on surface mineland. In Recovery and restoration of damaged ecosystems. Edited by J. Cairns, Jr., K.L. Dickson and E.E. Herricks. Univ. Virginia Press, Charlottesville.

Ritchey, K.D., Souza, D.M.G., Lobato, E. and Correa, O. 1980. Calcium leaching to increase rooting depth in a Brazilian savannah oxisol. Agron. J. 72(1): 40-44.

Ritchey, K.D., Silva, J.E. and Costa, U.F. 1982. Calcium deficiency in clayey B horizons of savannah oxisols. Soil Sci. 133: 378-382.

Ritchie, G.S.P., Posner, A.M. and Ritchie, I.M. 1980. The determination of trace levels of aluminum by differential pulse polarography. Anal. Chim. Acta 117: 233-239.

Roberts, D.A., Singer, R. and Boylen, C.W. 1985. The submersed macrophyte communities of Adirondack Lakes (New York, U.S.A.) of varying degrees of acidity. Aquat. Bot. 21: 219-235.

Roberts, D. and Singer, R. 1983. Personal communication. Dep. of Biology and Freshwater Institute, Rensselaer Polytechnic Institute, Troy, New York, and Dep. of Civil Engineering, Syracuse Univ., Syracuse, New York.

Robertson, J.A., Felsenfeld, A.J., Haygood, C.C., Wilson, P., Clarke, C. and Llach, F. 1983. Animal model of aluminum-induced osteomalacia: role of chronic renal failure. Kidney Int. 23: 327-335.

Roff, J.C. and Kwiatkowski, R.E. 1977. Zooplankton and zoobenthos communities of selected northern Ontario lakes of different acidities. Can. J. Zool. 55: 899-911.

Rorison, I.H. 1960a. Some experimental aspects of the calcicole-calcifuge problem. I. The effects of competition and mineral nutrition upon seedling growth in the field. J. Ecol. 48: 585-599.

Rorison, I.H. 1960b. Some experimental aspects of the calcicole-calcifuge problem. II. The effects of mineral nutrition on seedling growth in solution culture. J. Ecol. 48: 679-688.

Rorison, I.H. 1965. The effect of aluminum on the uptake and incorporation of phosphate by excised sanfoin roots. New Physiol. 64: 23-27.

Rosenberger, G.J., Smith, W.D., Miller, W.W. and Risby, T.H. 1979. Analysis of size-fractionated and time-dependent particulate matter for metals by atomic absorption spectrometry or by neutron activation analysis. Adv. Chem. Ser. 172: 40-53.

Ross, G.J., Ivarson, K.C. and Miles, N.M. 1982. Microbial formation of basic ferric sulfates in laboratory systems and in soils. Soil Sci. Soc. Am. Spec. Publ. 10: 77-94.

Rosseland, B.O. 1980. Physiological responses to acid water in fish. 2. Effects of acid water on metabolism and gill ventilation in brown trout, _Salmo_ _trutta_ L., and brook trout, _Salvelinus fontinalis_ Mitchill. _In_ Proc. Int. Conf. Ecological Impact Acid Precipitation, Norway. _Edited_ _by_ D. Drablos and A. Tollan. SNSF Project. pp. 348-349.

Rosseland, B.O. and Skogheim, O.K. 1984. A comparative study on salmonid fish species in acid aluminium-rich water. II. Physiological stress and mortality of one- and two-year-old fish. Rep. Inst. Freshwater Res. Drottningholm 61: 186-194.

Ruff, J.K. and Tyree, S.Y., Jr. 1958. Light scattering studies on aqueous aluminum nitrate solutions. J. Am. Chem. Soc. 80: 1523-1526.

Russell, E.W. (Editor.) 1973. Soil conditions and plant growth. 10th ed. Longman, New York.

Sadler, K. and Lynam, S. 1985. The mineral content of some freshwater invertebrates in relation to stream pH and calcium concentration. Central Electricity Research Laboratories, Leatherhead, Surrey, England. Manuscript Rep. TPRD/L/2781/N84. 15 pp.

Sampson, M., Clarkson, D. and Davies, D.D. 1965. DNA synthesis in aluminum-treated roots of barley. Science 148: 1476-1477.

Sanborn, N.H. 1945. The lethal effect of certain chemicals on fresh water fish. Canner 101(5): 13.

Sanderson, C.L., McLachlan, D.R.C. and De Boni, U. 1982. Altered steroid induced puffing by chromatin bound aluminum in a polytene chromosome of the black fly Simulium vittatum. Can. J. Genet. Cytol. 24(1): 27-36.

Sand-Jensen, K. and Rasmussen, L. 1978. Macrophytes and chemistry of acidic streams from lignite mining areas. Bot. Tidsskr. 72 (2-3): 105-112.

Sarkander, H.-I., Balb, G., Schlosser, H., Stoltenburg, G. and Lux, R.M. 1983. Blockade of neuronal brain RNA initiation sites by aluminum: a primary molecular mechanism of aluminum-induced neurofibrillary changes. In Brain aging: neuropathology and neuropharmacology. Edited by J. Cervos-Navarro and H.-I. Sarkander. Raven Press, New York. pp. 645-647.

Sartain, J.B. and Kamprath, E.J. 1978. Aluminum tolerance of soybean cultivars based on root elongation in solution culture compared with growth in acid soil. Agron. J. 70: 17-20.

Sastri, C.S., Petri, H. and Erdtmann, G. 1977. Determination of 13 elements with atomic numbers between 12 and 47 by 14-MeV helium-3 activation analysis. Anal. Chem. 49(11): 1510-1513.

Savage, J. 1973. Aluminum hydroxide granuloma. Proc. R. Soc. Med. 66(10): 984-985.

Schaut, G.G. 1939. Fish catastrophes during droughts. J. Am. Water Works Assoc. 31: 771.

Scheider, W.A., Jeffries, D.S. and Dillon, P.J. 1979. Effects of acidic precipitation on Precambrian freshwaters in southern Ontario, Canada. J. Great Lakes Res. 5(1): 45-51.

Schindler, D.W., Hesslein, R.H., Wagemann, R. and Broecker, W.S. 1980a. Effects of acidification on mobilization of heavy metals and radionuclides from the sediments of a freshwater lake. Can. J. Fish. Aquat. Sci. 37: 373-377.

Schindler, D.W., Wagemann, R., Cook, R.B., Ruszczynski, T. and Prokopowich, J. 1980b. Experimental acidification of Lake 223, Experimental Lakes Area: Background data and the first three years of acidification. Can. J. Fish. Aquat. Sci. 37: 342-354.

Schnitzer, M. 1969. Reactions between fulvic acid, a soil humic compound and inorganic soil constituents. Soil Sci. Soc. Am. J. 33: 75.

Schnitzer, M. 1971. Metal-organic matter interactions in soils and waters. *In* Organic compounds in aquatic environments. *Edited by* S.D. Faust and J.V. Hunter. Marcel Dekker, New York. pp. 297-313.

Schnitzer, M. and Skinner, S.I.M. 1963. Organo-metallic interactions in soils: I. Reactions between a number of metal ions and the organic matter of a podsol Bh horizon. Soil Sci. 96: 86-93.

Schoen, R. and Roberson, C.E. 1970. Structures of Al-OH (aluminum hydroxide) and geochemical implications. Am. Mineral. 55: 43-77.

Schofield, C.L. 1977. Acid snow-melt effects on water quality and fish survival in the Adirondack Mountains of New York state. Res. Proj. Tech. Compl. Rep., Proj. No. A-072-NY. Office of Water Research and Technology, U.S. Dep. of the Interior, Washington, D.C.

Schofield, C.L. and Trojnar, J.R. 1980. Aluminium toxicity to brook trout (*Salvelinus fontinalis*) in acidified waters. *In* Polluted rain. *Edited by* T.Y. Toribara, M.W. Miller and P.E. Morrow. Plenum Press, New York. pp. 341-366.

Schofield, R.K. and Taylor, A.W. 1954. The hydrolysis of Al salt solutions. J. Chem. Soc. London 1954: 4445-4448.

Schofield, C.L., Webster, D.A., Guthrie, C.A. and Flick, W.A. 1981. Management of acidified waters. Final report. Contract C-164480. New York Dep. Environ. Conserv. 82 pp.

Seip, H.M. 1980. Acidification of freshwaters: sources and mechanisms. *In* Proc. Int. Conf. Ecological Impact of Acid Precipitation, Norway. *Edited by* D. Drablos and A. Tollan. SNSF Project. pp. 358-366.

Seip, H. and Freedman, B. 1978. Effects of acid precipitation on soils. Meeting summary. *In* Effects of acid precipitation on terrestrial ecosystems. *Edited by* T.C. Hutchinson and M. Havas. Plenum Press, New York. pp. 591-596.

Seller, R.H. 1971. The role of magnesium in digitalis toxicity. Am. Heart J. 82: 551-556.

Shaver, C.G. and Riddell, A.R. 1947. Lung changes associated with the manufacture of alumina abrasives. J. Ind. Hyg. Toxicol. 29 (3): 147-157.

Shaw, P.G., McKown, D. and Manakan, E. 1981. Trace element determinations in shale oil products by neutron activation. Anal. Chim. Acta 123: 65-74.

Sheath, R.G., Havas, M., Hellebust, J.A. and Hutchinson, T.C. 1982. Effects of long-term natural acidification on the algal communities of tundra ponds at the Smoking Hills, N.W.T., Canada. Can. J. Bot. 60(1): 58-72.

Shields, J.B. and Mitchell, H.H. 1941. The effect of calcium and phosphorus on the metabolism of lead. J. Nutr. 21: 541-552.

Shike, M., Harrison, J.E., Sturtridge, W.C., Sturtridge, M.D., Tam, C.S., Bobechko, P.E., Jones, G., Murray, T.M. and Jeejeebhoy, K.N. 1980. Metallic bone disease in patients receiving long-term total parenteral nutrition. Ann. Intern. Med. 92: 343-350.

Shore, D., King, S.W., Kaye, W., Torrey, E.F., Winfrey, H.J., Potkin, S.G., Winberge, D.R., Savory, J., Willis, M.R. and Wyatt, M.R. 1980. Serum and cerebrospinal fluid aluminum and circulating parathyroid hormone in primary degenerative (senile) dementia. Neurotoxicology 1(4): 55-65.

Shorr, E. and Carter, A.C. 1950. Aluminum gels in the management of renal phosphatic calculi. J. Am. Med. Assoc. 144: 1542-1556.

Short, A.I.K., Winney, R.J. and Robson, J.S. 1980. Reversible microcytic hypochromic anaemia in dialysis patients due to aluminum intoxication. Proc. Eur. Dial. Transplant Assoc. 17: 226-233.

Sidwell, V.D., Loomis, A.L., Foncannon, P.R. and Buzzell, D.H. 1978. Composition of the edible portions of raw, fresh or frozen crustaceans, finfish and molluscs. Mar. Fish. Rev. 40(12): 1-16.

Siegel, N. and Haug, A. 1983. Aluminum interaction with calmodulin. Evidence for altered structure and function from optical and enzymatic studies. Biochim. Biophys. Acta 744: 36-45.

Sillén, L.G. 1954. On equilibria in systems with polynuclear complex formation: "Core and Links" complexes. Acta Chem. Scand. 8: 299-335.

Sillén, L.G. 1959. Quantitative studies of hydrolytic equilibria. Q. Rev. London 13: 146-148.

Sillén, L.G. and Martell, A.E. 1971. Stability constants of metal-ion complexes. Suppl. 1. Spec. Publ. 25. The Chemical Society, Burlington House, London.

Silvey, W.D. 1967. Occurrence of selected minor elements in the waters of California. Water Supply Pap. 1535-L. U.S. Geological Survey, Washington, D.C.

Simkiss, K. 1961. Calcium metabolism and avian reproduction. Biol. Rev. 36: 321-367.

Simpson, J.R., Pinkerton, A. and Lazdovskis, J. 1977. Effects of subsoil calcium on the root growth of some lucerne genotypes (Medicago sativa L.) in acidic soil profiles. Aust. J. Agric. Res. 28: 629-638.

Six, K.M. and Goyer, R.A. 1970. Experimental enhancement of lead toxicity by low dietary calcium. J. Lab. Clin. Med. 76: 933-942.

Skogheim, O.K. and Rosseland, B.O. 1984. A comparative study on salmonid fish species in acid aluminum-rich water. I. Mortality of eggs and alevins. Rep. Inst. Freshwater Res. Drottningholm 61: 176-185.

Skogheim, O.K., Rosseland, B.O. and Sevaldrud, I.H. 1984. Deaths of spawners of Atlantic salmon (Salmo salar L.) in River Ogna, S.W. Norway, caused by acidified aluminium-rich water. Rep. Inst. Freshwater Res. Drottningholm 61: 195-202.

Slater, D.N., Underwood, J.C.E., Durrant, T.E., Gray, T. and Hopper, I.P. 1982. Aluminum hydroxide granulomas: light and electron-microscopic studies and X-ray microanalysis. Br. J. Dermatol. 107: 103-108.

Smith, P.M. and Martell, A.E. 1976. Critical stability constants. Vol. 4. Plenum Press, New York.

Smith, R.W. 1969. The state of aluminum(III) in aqueous solution and adsorption of hydrolysis products on aluminum-oxide. Ph.D. Thesis, Stanford Univ., California. 194 pp.

Sommer, A.L. 1926. Studies concerning the essential nature of aluminum and silicon for plant growth. Univ. Calif. Berkeley Publ. Agric. Sci. 5: 57-81.

Sorenson, J.R.J., Campbell, I.R., Tepper, L.B. and Lingg, R.D. 1974. Aluminum in the environment and human health. Environ. Health Perspect. 8: 3-96.

Spencer, H., Kramer, L., Norris, C. and Osis, D. 1982. Effect of small doses of aluminum-containing antacids on calcium and phosphorus metabolism. Am. J. Nutr. 36: 32-40.

Sprules, W.G. 1975. Factors affecting the structure of limnetic crustacean zooplankton communities in central Ontario lakes. Verh. Int. Ver. Limnol. 19: 635-643.

Spry, D.J., Wood, C.M. and Hodson, P.V. 1981. The effect of environmental acid in freshwater fish with particular reference to the soft water lakes in Ontario and the modifying effects of heavy metals. A literature review. Can. Tech. Rep. Fish. Aquat. Sci. No. 999. 144 pp.

Stagg, G.V. and Millin, D.J. 1975. The nutritional and therapeutic value of tea - a review. J. Sci. Food Agric. 26: 1439-1459.

Steiner, K.C., McCormick, L.H. and Canavera, D.J. 1980. Differential response of paper birch provenances to aluminum in solution culture. Can. J. For. Res. 10: 25-29.

Stokes, P.M. 1985. Personal communication. Institute for Environmental Studies, Univ. of Toronto, Toronto, Ontario.

Stokes, P.M., Turner, P. and Havas, M. 1985. Unpublished data. Institute for Environmental Studies, Univ. of Toronto, Toronto, Ontario.

Stoklasa, J. 1922. Uber der Verbreitung der Aluminiums in der natur und seine Bedeutung beim bau-und Betreibstoffweschsel der Pflanzen. G. Fischer, Jona.

Stol, R.I., Van Helden, A.K. and de Bruyn, P.L. 1976. Hydrolysis - precipitation studies of Al(III) solutions. 2. A kinetic study and model. J. Colloid Interface Sci. 57(1): 115-131.

Stumm, W. and Morgan, J.J. 1981. Aquatic chemistry: an introduction emphasizing chemical equilibria in natural waters. 2nd ed. Wiley, New York. 780 pp.

Sturgeon, R.E. 1977. Factors affecting atomization and measurement in graphite furnace atomic absorption spectrometry. Anal. Chem. 49(14): 1255A-1267A.

Sturman, J.A., Wisniewski, H.M. and Shek, J.W. 1983. High affinity uptake of gamma amino butyric acid and glycine by rabbits with aluminum induced neurofibrillary changes. Neurochem. Res. 8(9): 1097-1110.

Subramanian, K.S., Chakrabarti, C.L., Sueiras, J.E. and Maines, I.S. 1978. Preservation of some trace metals in samples of natural waters. Anal. Chem. 50(3): 444-448.

Sullivan, J.H. and Singley, J.E. 1968. Reactions of metal ions in dilute aqueous solutions: Hydrolysis of aluminum. J. Am. Water Works Assoc. 60: 1280-1287.

Szabo, Z.G., Csanyi, L.J. and Kavai, M. 1955. Bestimmung der Loeslichkeitsprodukte von Metallhydroxydniederschlaegen. 1. Ueber die Reaktion des Aluminium-Ions mit dem Hydroxyl-Ion. Z. Anal. Chem. 146: 401-404.

Tabata, K. 1969. Studies on the toxicity of heavy metals to aquatic animals and the factors to decrease the toxicity. I. On the formation and the toxicity of precipitates of heavy metals. Tokaiku Suisan Kenkyusho Kenkyu Hokoku 58: 203.

Tanabe, H. 1954. Aluminium compounds. II. Composition of basic aluminum solution. J. Pharm. Soc. Jpn. 74: 866-872.

Tanaka, A. and Navasero, S.A. 1966. Aluminum toxicity of the rice plant under water culture conditions. Soil Sci. Plant Nutr. 12: 55-60.

Tanner, T.M., Young, J.A. and Cooper, J.A. 1974. Multielement analysis of St. Louis aerosols by nondestructive techniques. Chemosphere 3(5): 75-78.

Terry, R.D. and Pena, C. 1965. Experimental production of neurofibrillary degeneration. 2. Electron microscopic, phosphatase histochemistry and electron probe analysis. J. Neuropathol. Exp. Neurol. 24: 200-210.

Teulon, F. and Simeon, C. 1966. Toxicological tests of chemical products on freshwater fish. Rapport CEA-R2938, Commissariat à l'Energie Atomique, April.

Theobald, P.K., Jr., Lakin, H.W. and Hawkins, D.B. 1963. The precipitation of aluminum, iron and manganese at the junction of Deer Creek with the Snake River in Summit County, Colorado. Geochim. Cosmochim. Acta 27: 121-132.

Theriault, G., De Guire, L. and Cordier, S. 1981. Reducing aluminum, an occupation possibly associated with bladder cancer. Can. Med. Assoc. J. 124(4): 419-422, 425.

Thomas, A. 1915. Effects of certain metallic salts upon fishes. Trans. Am. Fish. Soc. 44: 121.

Thomas, G.W. 1975. The relationship between organic matter content and exchangeable aluminum in an acid soil. Soil Sci. Soc. Am. Proc. 35: 591.

Thompson, G.W. and Moore, R.J. 1981. The effect of aluminum and manganese on the growth of selected mycorrhizal fungi. In Proc. 5th North American Conference on Mycorrhizae, Aug. 16-21, Quebec.

Toda, W., Lux, J. and Van Loon, J.C. 1980. Determination of aluminum in solution from gel filtration chromatography of human serum by electrothermal atomic absorption spectroscopy. Anal. Lett. 13(B13): 1105-1113.

Tong, S.S.C., Morse, R.A., Bache, C.A. and Lisk, D.J. 1975. Elemental analysis of honey as an indicator of pollution. Arch. Environ. Health 30: 329-332.

Tornheim, K., Gilbert, T.R. and Lowenstein, J.M. 1980. Metal contaminants in commercial preparations of nucleotides. Anal. Biochem. 103(1): 87-93.

Touam, M., Martinez, F., Lacour, B., Bourdon, R., Zingraff, J., Di Guilio, S. and Drueke, T. 1983. Aluminum-induced, reversible microcytic anemia in chronic renal failure: clinical and reexperimental studies. Clin. Nephrol. 19: 295-298.

Trapp, G.A. 1980. Aluminum interaction with enzymes and proteins. Inhibition of hexokinase. Neurotoxicology 1(4): 89-100.

Trapp, G.A. 1983. Plasma aluminum is bound to transferrin. Life Sci. 33(4): 311-316.

Trapp, G.A., Miner, G.D., Zimmerman, R.L., Mastri, A.R. and Heston, L.L. 1978. Aluminum levels in brain in Alzheimer's disease. Biol. Psychol. 13: 709-718.

Truchet, M. 1976. Electron- and ion-microprobe determination of natural accumulation of aluminum in nuclei of diverse cell types. C.R. Acad. Sci. Ser. D 282(20): 1785-1788.

Tsunoda, K.I., Fujiwara, K. and Fuwa, K. 1977. Subnanogram fluorine determination by aluminum monofluoride molecular absorption spectrometry. A review. Anal. Chem. 49(13): 2035-2039.

Turner, R.C. 1968. Conditions in solution during the formation of gibbsite in dilute Al salt solutions: II. Effect of length of time of reaction on the formation of poly-nuclear hydroxy-aluminum cations, the substitution of other anions for OH^- in amorphous $Al(OH)_3$ and the crystallization of gibbsite. Soil Sci. 106: 291-296.

Turner, R.C. 1969. Three forms of aluminum in aqueous systems determined by 8-quinolinate extraction methods. Can. J. Chem. 47: 2521-2527.

Turner, R.C. 1971. Kinetics of reactions of 8-quinolinol and acetate with hydroxyaluminum species in aqueous solutions. 2. Initial solid phases. Can. J. Chem. 49: 1688-1690.

Turner, R.C. 1975. The equilibrium constant for the formation of $Al_2(OH)_2^{4+}$ in aqueous solutions. Can. J. Chem. 53(19): 2811-2817.

Turner, R.C. 1976. Effect of aging on properties of polynuclear hydroxyaluminum cations. Can. J. Chem. 54: 1524-1534.

Turner, R.C. and Sularman, W. 1971. Kinetics of reaction of 8-quinolinol and acetate with hydroxyaluminum species in aqueous solutions. 1. Polynuclear hydroxyaluminum cations. Can. J. Chem. 49: 1683-1687.

Udenfriend, S. 1962. Fluorescence assay in biology and medicine. Vol. I. Academic Press, New York. pp. 388-399.

Uéno, M. 1958. The disharmonious lakes of Japan. Verh. Int. Ver. Limnol. 13: 217-226.

Ujiie, R. 1959. Interference in bacterial metabolism by chelating agents. Mechanism of the antibacterial action of ethylenediaminetetraacetic acid. Nippon Saikingaku Zasshi 14: 105. (Chem. Abstr. 55, 1787, 1961.)

Ulrich, B. 1983. Soil acidity and its relation to acid deposition. In Effects of accumulation of air pollutants in forest ecosystems. Edited by B. Ulrich and J. Pankrath. D. Reidel Publ. Co., Boston. pp. 127-146.

Ulrich, B., Mayer, R. and Khanna, P.K. 1980. Chemical changes due to acid precipitation in a loess-derived soil in central Europe. Soil Sci. 130: 193-199.

Underwood, E.J. (Editor.) 1977. Trace elements in human and animal nutrition. 4th ed. Academic Press, New York.

Upitis, V., Nollendorfa, A. and Pakalne, D. 1975. Little-studied trace elements in Chlorella culture. Aluminum. Latv. P.S.R. Zinat. Akad. Vestis 3: 21.

Van Cauwelaert, F.H. and Bosmans, H.J. 1969. Polycations formés dans l'hydrolyse de l'ion aluminium. Rev. Chim. Minerale 6: 611-623.

Van Dam, H., Suurmond, G. and Braak, C.T. 1980. Impact of acid precipitation on diatoms and chemistry of Dutch moorland pools. In Proc. Int. Symp. Ecological Impact Acid Precipitation, Norway. Edited by D. Drablos and A. Tollan. SNSF Project. pp. 298-299.

Vangenechten, J.H.D. and Vanderborght, O.L.J. 1980. Acidification of Belgian moorland pools by acid sulphur-rich rainwater. In Proc. Int. Conf. Ecological Impact Acid Precipitation, Norway. Edited by D. Drablos and A. Tollan. SNSF Project. pp. 246-247.

Van Loon, J.C. 1979. Metal speciation by chromatography/atomic spectrometry. Anal. Chem. 51(11): 1139A-1150A.

Van Olphen, H. 1977. An introduction to clay colloid chemistry. 2nd ed. Wiley, New York. 336 pp.

Van Olphen, H. and Fripiat, J.J. (Editors.) 1979. Data handbook for clay materials and other non-metallic minerals. Pergamon Press, Oxford. 355 pp.

Varghese, Z., Moorhead, J.F. and Wills, M.R. 1973. Plasma calcium and magnesium fractions in chronic renal failure patients on maintenance haemodialysis. Lancet 2: 985-988.

Veitch, F.P. 1904. Comparison of methods for the estimation of acidity. Am. Chem. Soc. 26: 637-662.

Veith, J.A. 1977. Basicity of exchangeable aluminum, formation of gibbsite, and composition of exchange acidity in the presence of exchangers. Soil Sci. Soc. Am. J. 41(5): 865-870.

Veith, J.A. and Sposito, G. 1979. On the average equilibrium OH-Al molar ratio for aluminum adsorbed by a synthetic cation exchanger. Soil Sci. 127(3): 161-167.

Verbeelen, D., Smeyers-Verbeke, J. and Massarat, D.L. 1980. Aluminum (Al) containing antacids: source of high serum Al levels in patients treated with regular hemodialysis. Toxicol. Lett. 1: 61-68.

Versieck, J. and Cornelis, R. 1980. Measuring aluminum levels. New Engl. J. Med. 302(8): 468.

Viestra, R. and Haug, A. 1978. The effect of Al^{3+} on the physical properties of membranes in Thermoplasma acidophilum. Biochem. Biophys. Res. Commun. 84: 138.

Vose, P.B. and Randall, P.J. 1962. Resistance to aluminum and manganese toxicities in plants related to variety and cation exchange capacity. Nature (London) 4849: 85-86.

Wagemann, R. and Brunskill, G.J. 1975. The effect of filter pore size on analytical concentrations of some trace elements in filtrates of natural water. Int. J. Environ. Anal. Chem. 4(1): 75-84.

Wallace, S.U. and Anderson, I.C. 1984. Aluminum toxicity and DNA synthesis in wheat roots. Agron. J. 76: 5-8.

Wallen, I.E., Greer, W.C. and Lasater, R. 1957. Toxicity to Gambusia affinis of certain pure chemicals in turbid waters. Sewage Ind. Wastes 29: 695.

Wallihan, E.F. 1948. The influence of aluminum on the phosphorus nutrition of plants. Am. J. Bot. 35: 106-112.

Wang, H.S. 1977. In Aging and dementia. Edited by W.L. Smith and M. Kinsbourne. Spectrum Publ., New York. pp. 1-24.

Ward, M.K., Feest, T.G., Ellis, H.A., Parkinson, I.S., Kerr, D.N.S., Herrington, J. and Goode, G.L. 1978. Osteomalacic dialysis osteodystrophy: evidence for a water-borne aetiological agent, probably aluminum. Lancet 1: 841-845.

Warner, R.W. 1971. Distribution of biota in a stream polluted by acid mine-drainage. Ohio J. Sci. 71: 202-215.

Washko, P.W. and Cousins, R.J. 1977. Role of dietary calcium and calcium binding protein in cadmium toxicity in rats. J. Nutr. 107: 920-928.

Wasserman, R.H. 1962. Studies on vitamin D_3 and the intestinal absorption of calcium and other ions in the rachitic chick. J. Nutr. 77: 69-80.

Weeks, S.J., Haraguchi, H. and Winefordner, J.D. 1978. Improvement of detection limits in laser-excited atomic fluorescence flame spectrometry. Anal. Chem. 50(2): 360-368.

Weigelt, C., Saare, O. and Schwab, L. 1885. The damage to fisheries and fish culture by industrial and domestic sewage. Arch. Hyg. 3: 39.

Weiss, G.B. and Goodman, F.R. 1969. Effects of lanthanum on contraction, calcium distribution and 45-Ca movements in intestinal smooth muscle. J. Pharmacol. Exp. Ther. 169: 46-55.

Welch, C.D. and Nelson, W.L. 1950. Calcium and magnesium requirements of soybeans as related to the degree of base saturation of the soil. Agron. J. 42: 9-13.

Whitby, L.M. and Hutchinson, T.C. 1974. Heavy-metal pollution in the Sudbury mining and smelting region of Canada. II. Soil toxicity tests. Environ. Conserv. 1: 191-200.

Wiklander, L. 1980. Interaction between cations and anions influencing adsorption and leaching. *In* Effects of acid precipitation on terrestrial ecosystems. *Edited by* T.C. Hutchinson and M. Havas. Plenum Press, New York. pp. 239-254.

Wile, I. and Miller, G. 1983. The macrophyte flora of 46 acidified and acid-sensitive soft water lakes in Ontario. Limnology Section, Ontario Ministry of the Environment, Rexdale, Ontario.

Williams, P., Khanna, R. and Crapper McLachlan, D.R. 1981. Enhancement of removal of aluminum by desferrioxamine in a patient on continuous ambulatory peritoneal dialysis with dementia. Periton. Dial. Bull. No. 1.

Wills, M.R. and Savory, J. 1983. Aluminum poisoning: dialysis encephalopathy, osteomalacia, and anaemia. Lancet 2: 29-33.

Wing, A.J., Brunner, C.P., Brynger, H., Chatler, C., Donckerwolocke, B.A., Gurland, H.J., Jacobs, C., Kramer, P. and Selwood, N.H. 1980. Dialysis dementia in Europe: Report from the European dialysis and transplant association. Lancet 2: 190-192.

Wisniewski, H.M., Narang, H.K. and Terry, R.D. 1976. Neurofibrillary tangles of paired helical filaments. J. Neurol. Sci. 27(2): 173-181.

Wolcott, A.R., Foth, H.D., Davis, J.F. and Shickluna, J.C. 1965. Nitrogen carriers: soil effects. Soil Sci. Soc. Am. Proc. 29: 405-410.

Wong, P.C.L., Lai, J.C.K., Lim, L. and Davison, A.N. 1981. Selective inhibition of L-glutamate and gamma amino butyrate transport in nerve ending particles by aluminum chloride, manganese chloride and cadmium chloride. J. Inorg. Biochem. 14(3): 253-260.

Wood, M., Cooper, J.E. and Holding, A.J. 1984. Aluminum toxicity and nodulation of *Trifolium repens*. Plant Soil 78: 381-391.

Woolrich, P.F. 1973. Occurrence of trace metals in the environment. An overview. Am. Ind. Hyg. Assoc. J. 34: 217-226.

Worker, N.A. and Migicovsky, B.B. 1961a. Effect of vitamin D on the utilization of zinc, cadmium and mercury in the chick. J. Nutr. 75: 222-224.

Worker, N.A. and Migikovsky, B.B. 1961b. Effect of vitamin D on the utilization of beryllium, magnesium, calcium, strontium and barium in the chick. J. Nutr. 74: 490-494.

Wright, R.F., Conroy, N., Dickson, W.T., Harriman, R., Henriksen, A. and Schofield, C.L. 1980a. Acidified lake districts of the world: A comparison of water chemistry of lakes in southern Norway, southern Sweden, southwestern Scotland, the Adirondack Mountains of New York, and southeastern Ontario. In Proc. Int. Conf. Ecological Impact Acid Precipitation, Norway. Edited by D. Drablos and A. Tollan. SNSF Project. pp. 377-379.

Wright, R.F., Harriman, R., Henriksen, A., Morrison, B. and Caines, L.A. 1980b. Acid lakes and streams in the Galloway area, southwestern Scotland. In Proc. Int. Conf. Ecological Impact Acid Precipitation, Norway. Edited by D. Drablos and A. Tollan. SNSF Project. pp. 248-249.

Yan, N.D. and Stokes, P. 1978. Phytoplankton of an acidic lake, and its responses to experimental alterations of pH. Environ. Conserv. 5: 93-100.

Yan, N.D., Scheider, W.A. and Dillon, P.J. 1977. Chemical and biological changes in Nelson Lake, Ontario following experimental elevation of lake pH. Water Pollut. Res. 12: 213-231.

Yan, N.D., Lafrance, C.J. and Hitchin, G.G. 1982. Planktonic fluctuations in a fertilized acidic lake: the role of invertebrate predators. In Acid rain/fisheries. Edited by R.E. Johnson. Am. Fish. Soc., Bethesda, Maryland. pp. 137-154.

Yase, Y. 1977. The basis process of amyotrophic lateral sclerosis as reflected in Kii Peninsula and Guam. Excerpta Med. Int. Congr. Ser. 434: 43.

Yase, Y., Yoshimasu, F., Uebayashi, Y., Iwata, S. and Kimura, K. 1974. Amyotrophic lateral sclerosis: interaction of divalent metals in central nervous system tissue and soft tissue calcification. Proc. Jpn. Acad. 50(7): 401-406.

Yates, C.M., Simpson, J., Russell, D. and Gordon, A. 1980. Cholinergic enzymes neurofibrillary degeneration produced by aluminum. Brain Res. 197: 269-274.

Yoshimasu, F., Nebayaski, Y., Iwata, W. and Sassajima, K. 1976. Studies on amyotrophic lateral sclerosis by neutron activation and analysis. Folia Psychiatr. Neurol. Jpn. 30: 49-55.

Young, R.S. 1980. Separation procedures in inorganic analysis. A practical handbook. Wiley, New York. pp. 1-20.

Zief, M. and Mitchell, J.W. 1976. Contamination control in trace element analysis. John Wiley, New York. 262 pp.

Zoller, W.H. and Gordon, G.E. 1970. Instrumental neutron activation analysis of atmospheric pollutants utilizing Ge(Li) gamma ray detectors. Anal. Chem. 42: 257-265.

Zwarun, A.A. and Thomas, G.W. 1973. Effect of soluble and exchangeable aluminum on Pseudomonas stutzeri. Soil Sci. Soc. Am. Proc. 37(3): 386-387.

PUBLICATIONS

of the
du

Environmental Secretariat
Secrétariat de l'environnement

NRCC Associate Committee on Scientific Criteria for Environmental Quality
CNRC-Comité associé sur les critères scientifiques concernant l'état de l'environnement

NRCC No. CNRC n°	
12678	Inventory of Pollution-Relevant Research in Canada. Interim Report, Vols. 1, 2. Etat de recherches sur la pollution au Canada. Rapport provisoire, Tomes 1, 2. 1972. 310 pp. $6.50. (Out of print - Edition épuisée)
14108	Inventory of Pollution-Relevant Research in Canada. Vols. 3, 4. Etat de recherches sur la pollution au Canada. Tomes 3, 4. 1975. 558 pp. $6.50.
12226	Environmental Fluoride (Special Report). 1971. 39 pp.
12226	Le fluor dans l'environnement. 1971. 41 pp.
13079	Detection and Inactivation of Enteroviruses in Water. 1973. 26 pp. $1.25.
13080	Problems and Selection of Topics for Compilation of Cause/Effect Data. 1973. 51 pp. $1.25.
13236	Détection et inactivation des entérovirus dans l'eau. 1973. 30 pp. $1.25.
13339	Problèmes et choix de thèmes en vue d'une compilation de données cause/effet. 1974. 45 pp. $1.25.
13501	The Effects of Pulp and Paper Wastes on Aquatic Life with Particular Attention to Fish and Bioassay Procedures for Assessment of Harmful Effects. 1973. 60 pp. $2.50.
13502	L'effet des déchets de pâtes et papier sur la vie aquatique. 1974. 75 pp. $2.50.
13566	A Criteria Digest on Radioactivity in the Environment. 1974. 53 pp. $1.50.
13567	Un résumé de critères sur la radioactivité dans l'environnement. 1974. 45 pp. $1.50.
13682	Lead in the Canadian Environment. 1973. 116 pp. $2.00. (Out of print - See NRCC 16736).
13683	Le plomb dans l'environnement canadien. 1973. 130 pp. $2.00. (Edition épuisée - voir CNRC 16737).
13684	Picloram: The Effects of Its Use as a Herbicide on Environmental Quality. 1974. 128 pp. $5.00.
13685	Piclorame: les effets de son utilisation comme herbicide sur l'état de l'environnement. 1974. 130 pp. $1.00.
13686	A Method of Monitoring Nationally for Possible Delayed Effects of Various Occupational Environments. 1974. 42 pp. $1.25.
13687	Une méthode de surveillance nationale des effets possibles, à long terme, du milieu professionnel sur la santé. 1974. 40 pp. $1.25.
13688	Environmental Cause/Effect Phenomena Relating to Technological Development in the Canadian Arctic. 1974. 125 pp. $2.00.
13689	Phénomènes environnementaux de cause à effet liés au progrès technique dans l'arctique. 1974. 128 pp. $2.00.
13690	The Application of the Phosphorus Loading Concept to Eutrophication Research. 1974. 42 pp. $1.25.
13691	Application du concept de la vitesse d'apport de phosphore par unité de surface à la recherche sur l'eutrophisation. 1974. 44 pp. $1.25.

Available through prepaid purchase orders from

En vente, moyennant commandes prepayées, au Service des

Publications, NRCC/CNRC
Ottawa, Ontario K1A 0R6

NRCC No. CNRC n°	
14094	Chlordane: Its Effects on Canadian Ecosystems and Its Chemistry. 1974. 189 pp. $1.00.
14095	Chlordane: ses effets sur les ecosystèmes canadiens et sa chimie. 1975. 192 pp. $1.00.
14096	Photochemical Air Pollution: Formation, Transport and Effects. 1975. 224 pp. $2.50.
14097	La pollution photochimique de l'air: sa formation, son transport et ses effets. 1976. 203 pp. $2.50.
14098	Endosulfan: Its Effects on Environmental Quality. 1975. 100 pp. $1.25.
14099	Endosulfan: ses effets sur l'état de l'environnement. 1976. 98 pp. $1.25.
14100	Waterborne Dissolved Oxygen Requirements and Criteria With Particular Emphasis on the Canadian Environment. 1975. 111 pp. $2.00.
14101	Exigences et critères relatifs à l'oxygène dissous dans l'eau, et leurs particularités à l'environnement canadien. 1976. 111 pp. $2.00.
14102	Methoxychlor: Its Effects on Environmental Quality. 1975. 164 pp. $2.00.
14103	Méthoxychlore: ses effets sur l'état de l'environnement. 1976. 161 pp. $2.00.
14104	Fenitrothion: The Effects of Its Use on Environmental Quality and Its Chemistry. 1975. 162 pp. $2.00.
14105	Fénitrothion: effets de son utilisation sur l'état de l'environnement, et sa chimie. 1976. 164 pp. $2.00.
14106	Arboviruses and Human Health in Canada. 1975. 35 pp. $1.25.
14107	Arbovirus pathogènes au Canada. 1976. 40 pp. $1.25.
14109	Waste Heat in the Aquatic Environment. 1975. 40 pp. $1.00.
14110	Pollution thermique de l'environnement aquatique. 1976. 58 pp. $1.00.
15015	Sulphur and Its Inorganic Derivatives in the Canadian Environment. 1977. 426 pp. $5.00.
15016	Le soufre et ses dérivés minéraux dans l'environnement canadien. 1978. 441 pp. $5.00.
15017	Effects of Chromium in the Canadian Environment. 1976. 168 pp. $2.00.
15018	Les effets du chrome dans l'environnement canadien. 1977. 162 pp. $2.00.
15019	The Effects of Alkali Halides in the Canadian Environment. 1977. 171 pp. $2.00.
15020	Les effets des halogénures alcalins dans l'environnement canadien. 1977. 171 pp. $2.00.
15021	The Effects of Petroleum Refinery Liquid Wastes on Aquatic Life, with Special Emphasis on the Canadian Environment. 1976. 77 pp. $2.00.
15022	Les effets des déchets liquides du raffinage du pétrole sur la vie aquatique, particulièrement dans l'environnement canadien. 1977. 86 pp. $2.00.
15023	NTA (Nitrilotriacetic Acid) - An Ecological Appraisal. 1976. 46 pp. $1.25.
15024	NTA (acide nitrilotriacétique) - une analyse écologique. 1977. 48 pp. $1.25.
15383	Effects of Noise on Man. 1976. 87 pp. $2.50.
15384	Les effets du bruit sur l'homme. 1977. 92 pp. $2.50.
15385	*Bacillus thuringiensis*: Its Effects on Environmental Quality. 1976. 133 pp. $2.00.
15386	*Bacillus thuringiensis*: ses effets sur l'état de l'environnement. 1977. 127 pp. $2.00.
15387	Medicare Data: Its Use in Defining the Effects of the Environment on Health. 1977. 164 pp. $2.50.
15388	Les statistiques de l'assurance-maladie et leur rôle dans la définition de l'influence de l'environnement sur la santé. 1978. 166 pp. $2.50.

NRCC No. CNRC n°	
15389	Fenitrothion: The Long Term Effects of Its Use in Forest Ecosystems - Current Status. 1977. 18 pp. $1.00.
16074	Fénitrothion: effets à long terme de son utilisation dans les écosystèmes forestiers - situation actuelle. 1977. 20 pp. $1.00.
15391	Effects of Arsenic in the Canadian Environment. 1978. 363 pp. $2.00.
15392	Les effets de l'arsenic sur l'environnement canadien. 1979. 415 pp. $2.00.
16073	Proceedings of a Symposium on Fenitrothion: The Long-Term Effects of Its Use in Forest Ecosystems. Comptes rendus du symposium sur le fénitrothion: les effets à long terme de son utilisation dans les écosystèmes forestiers. 1977. 628 pp. $10.00.
16075	Phenoxy Herbicides: Their Effects on Environmental Quality with Accompanying Scientific Criteria for 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD). 1978. 440 pp. $10.00.
16076	Herbicides phénoxy - analyse de leurs effets sur l'état de l'environnement accompagnée de critères scientifiques à l'égard de la 2,3,7,8-tétrachlorodibenzo-p-dioxine (TCDD). 1979. 452 pp. $2.00.
16077	Polychlorinated Biphenyls: Biological Criteria for an Assessment of Their Effects on Environmental Quality. 1978. 172 pp. $2.00.
16078	Polychlorobiphényles: critères biologiques pour évaluer leurs effets sur l'état de l'environnement. 1979. 208 pp. $2.00.
16079	Ecotoxicology of Chlorpyrifos. 1978. 314 pp. $2.00.
16080	Ecotoxicologie du chlorpyrifos. 1979. 250 pp. $2.00.
16081	Environmental Fluoride 1977. 1978. 152 pp. $5.00.
16082	Le fluorure dans l'environnement, 1977. 1979. 175 pp. $2.00.
16446	Effects of Ultraviolet Radiation on Man. 1978. 90 pp. $2.00.
16447	Les effets du rayonnement ultraviolet sur l'homme. 1979. 91 pp. $2.00.
16448	The Biological Effects of Radio-frequency and Microwave Radiation. 1979. 244 pp. $5.00.
16449	Effets biologiques des radiofréquences et des micro-ondes. 1980. 244 pp. $5.00.
16450	The Aqueous Chlorination of Organic Compounds: Chemical Reactivity and Effects on Environmental Quality. 1978. 136 pp. $5.00.
16451	Chloration en milieu aqueux de composés organiques: réactivité chimique et effets sur l'état de l'environnement. 1979. 149 pp. $2.00.
16452	Effects of Asbestos in the Canadian Environment. 1979. 185 pp. $3.00.
16453	Les effets de l'amiante dans l'environnement au Canada. 1980. 202 pp. $3.00.
16454	Copper in the Aquatic Environment: Chemistry, Distribution, and Toxicology. 1979. 227 pp. $3.00.
16455	Le cuivre dans l'environnement aquatique: chimie, répartition et toxicologie. 1980. 249 pp. $3.00.
16736	Effects of Lead in the Environment - 1978. Quantitative Aspects. 1979. 779 pp. $10.00.
16737	Effets du plomb dans l'environnement - 1978. Aspects quantitatifs. 1980. 853 pp. $5.00.
16738	Report of a Special Conference on Hearing Threshold Levels of "Isolated" Human Populations. Comptes rendus du symposium spécial sur les niveaux d'audition des populations humaines "isolées". 1978. 104 pp. $3.00.
16739	Effects of Mercury in the Canadian Environment. 1979. 290 pp. $3.00.
16742	Effets du mercure dans l'environnement au Canada. 1980. 292 pp. $3.00.

NRCC No. CNRC n°	
16740	Carbofuran: Criteria for Interpreting the Effects of Its Use on Environmental Quality. 1979. 191 pp. $2.00.
16741	Carbofurane: critères pour interpréter les effets de son utilisation sur l'état de l'environnement. 1980. 184 pp. $2.00.
16743	Effects of Cadmium in the Canadian Environment. 1979. 148 pp. $5.00.
16744	Les effets du cadmium dans l'environnement canadien. 1979. 150 pp. $3.00.
16745	Effects of Lead in the Canadian Environment - 1978. Executive Report. Effets du plomb dans l'environnement canadien - 1978. Rapport administratif. 1979. 24 pp. $1.00.
17581	Water Hardness, Human Health, and the Importance of Magnesium. 1979. 119 pp. $3.00.
17582	Dureté de l'eau, santé et importance du magnésium. 1980. 123 pp. $3.00.
17583	Phthalate Esters in the Aquatic Environment. 1980. 108 pp. $3.00.
17584	Esters phtaliques dans l'environnement aquatique. 1981. 110 pp. $3.00.
17585	Executive Reports: Effects of Chromium, Alkali Halides, Arsenic, Asbestos, Mercury, and Cadmium in the Canadian Environment. 80 pp. Rapports Administratifs: effets du chrome, des halogénures alcalins, de l'arsenic, de l'amiante, du mercure, et du cadmium sur l'environnement canadien. 92 pp. 1980. $3.00.
17586	A Case Study of a Spill of Industrial Chemicals - Polychlorinated Biphenyls and Chlorinated Benzenes. 1980. $5.00.
17587	Effects of Yellow Phosphorus in the Canadian Environment. 1981. 110 pp. $3.00.
17588	Effets du phosphore blanc sur l'environnement canadien. 1981. 112 pp. $3.00.
17589	Zinc in the Aquatic Environment: Chemistry, Distribution, and Toxicology. 1981. 145 pp. $3.00.
17590	Le zinc dans l'environnement aquatique: chimie, répartition et toxicologie. 1981. 152 pp. $3.00.
18128	Intestinal Parasites of Man in the Canadian Environment. 1980. 69 pp. $2.00.
18129	Les parasites intestinaux de l'homme dans l'environnement canadien. 1980. 70 pp. $2.00.
18130	The Ecological Consequences of Dredging and Dredge Spoil Disposal in Canadian Waters. 1982. 142 pp. $5.00.
18131	Les conséquences écologiques du dragage et de l'élimination des résidus du dragage dans les eaux canadiennes. 1983. 150 pp. $5.00.
18132	Effects of Vanadium in the Canadian Environment. 1980. 94 pp. $2.00.
18133	Effets du vanadium dans l'environnement canadien. 1981. 92 pp. $2.00.
18134	Radioactivity in the Canadian Environment. 1980. 129 pp. $3.00.
18135	La radioactivité dans l'environnement canadien. 1981. 133 pp. $3.00.
18156	The Report of the ad hoc Panel Convened by the National Research Council of Canada to Review the Spill of Polychlorinated Biphenyls at the Federal Pioneer Ltd. Site in Regina, Saskatchewan. 30 January 1980. 15 pp.
18467	Hydrogen Sulfide in the Atmospheric Environment: Scientific Criteria for Assessing its Effects on Environmental Quality. 1981. 196 pp. $5.00.
18468	Sulfure d'hydrogène dans l'environnement atmospherique: critères scientifiques pour évaluer ses effets sur la qualité de l'environnement. 1982. 204 pp. $5.00.

NRCC No. CNRC n°	
18469	Ethylenethiourea: Criteria for the Assessment of its Effects on Man. 1980. 149 pp. $3.00.
18470	Ethylène-thiourée: critères pour évaluer ses effets sur l'homme. 1981. 187 pp. $3.00.
18471	Pesticide-Pollinator Interactions. 1981. 190 pp. $5.00.
18472	Interactions entre pesticides et pollinisateurs. 1981. 223 pp. $5.00.
18473	Effects of Aerosols on Atmospheric Processes. 1982. 208 pp. $8.00.
18474	Effets des aérosols sur les processus atmosphériques. 1983. 230 pp. $8.00.
18475	Acidification in the Canadian Aquatic Environment: Scientific Criteria for Assessing the Effects of Acidic Deposition on Aquatic Ecosystems. 1981. 369 pp. $10.00.
18476	Acidification dans l'environnement aquatique au Canada: critères scientifiques pour évaluer les effets du dépôt acide sur les écosystèmes aquatiques. 1982. 377 pp. $10.00.
18564	Effects of Inhaled Particles on Human Health: Influence of Particle Size and Shape. 1982. 177 pp. $8.00.
18565	Effets sur la santé des particules absorbées par voie respiratoire: influence de leur taille et de leur forme. 1983. 195 pp. $8.00
18566	Thermal Effects Upon Fishes. 1982. 200 pp. $8.00.
18567	Effets de la pollution thermique sur les poissons. 1983. 210 pp. $8.00.
18568	Effects of Nickel in the Canadian Environment. 1981. 352 pp. $4.00.
18569	Effets du nickel sur l'environnement canadien. 1982. 347 pp. $4.00.
18570	A Screen for the Relative Persistence of Lipophilic Organic Chemicals in Aquatic Ecosystems - An Analysis of the Role of a Simple Computer Model in Screening. I. A Simple Computer Model as a Screen for Persistence. II. An Introduction to Process Analyses and Their Use in Preliminary Screens of Chemical Persistence. 1981. 302 pp. $8.00.
18571	Contrôle de la persistance relative de produits organiques lipophiles dans les écosystèmes aquatiques - analyse du rôle d'une simple simulation par ordinateur. 1982. 335 pp. $8.00.
18572	Effects of Propoxur on Environmental Quality with Particular Reference to its Use for Control of Biting Flies. 1982. 238 pp. $8.00.
18573	Les effets du propoxur sur la qualité de l'environnement, notamment quant à son emploi dans la lutte contre les insectes piqueurs. 1982. 253 pp. $8.00.
18574	Polychlorinated Dibenzo-p-Dioxins: Criteria for Their Effects on Man and his Environment. 1981. 251 pp. $8.00.
18575	Polychlorodibenzo-p-dioxines: critères relatifs à leurs effets sur l'homme et son environnement. 1982. 276 pp. $8.00.
18576	Polychlorinated Dibenzo-p-Dioxins: Limitations to the Current Analytical Techniques. 1981. 184 pp. $8.00.
18577	Polychlorodibenzo-p-dioxines: limites des méthodes analytiques actuelles. 1982. 186 pp. $8.00.
18578	Chlorinated Phenols: Criteria for Environmental Quality. 1982. 191 pp. $8.00.
18579	Chlorophénols: critères pour évaluer leurs effets sur l'état de l'environnement. 1982. 217 pp. $8.00.
18976	Farm Animal Manures in the Canadian Environment. 1983. 139 pp. $8.00
18977	L'effet du fumier dans l'environnement canadien. 1983. 145 pp. $8.00
18978	Workshop on the Combined Effects of Xenobiotics. Atelier sur les effets combinés des xenobiotiques. 1982. 253 pp. $8.00.

NRCC No. CNRC n^o	
18979	Aminocarb: The Effects of its Use on the Forest and the Human Environment. 1982. 253 pp. $8.00.
18980	Aminocarbe: effets de son utilisation sur la forêt et l'environnement. 1983. 271 pp. $8.00
18981	Polycyclic Aromatic Hydrocarbons in the Aquatic Environment: Formation, Sources, Fate and Effects on Aquatic Biota. 1983. 209 pp. $8.00
18982	Les hydrocarbures aromatiques polycycliques dans le milieu aquatique: formation, sources, devenir et effets sur le biote aquatique. 1984. 218 pp. $8.00
18983	The Need for New Directions in Toxicological Funding. Le besoin d'une nouvelle politique en ce qui concerne les subventions dans le domaine toxicologique. 1982. 11 pp. $2.00.
19244	Ultrasound: Characteristics and Biological Action. 1981. 284 pp. $8.00.
19245	Les ultrasons: caractéristiques et action biologique. 1982. 284 pp. $8.00.
19246	The Effects of Cyanides on Aquatic Organisms with Emphasis upon Freshwater Fishes. 1982. 139 pp. $5.00.
19247	Effets des cyanures sur les organismes aquatiques, notamment sur les poissons d'eau douce. 1983. 144 pp. $5.00.
19248	Biting Flies in Canada: Health Effects and Economic Consequences. 1982. 157 pp. $5.00.
19249	Insectes piqueurs au Canada: effets sur la santé et conséquences économiques. 1983. 169 pp. $5.00.
19250	Radioactivity in the Canadian Aquatic Environment. 1983. 292 pp. $8.00
19251	La radioactivité dans l'environnement aquatique au Canada. 1983. 292 pp. $8.00
19252	Data Sheets on Selected Toxic Elements. 1982. 61 pp. $5.00.
19253	Fiches de données sur certains éléments toxiques. 1983. 48 pp. $5.00
20640	Cold: Special Aspects in the Canadian North. 1983. 33 pp. $3.00.
20641	Aspects particuliers du froid dans le nord canadien. 1983. 33 pp. $3.00
20642	Proceedings of a Symposium on Monitoring and Assessment of Airborne Pollutants with Special Emphasis on Long-range Transport and Deposition of Acidic Materials and Workshop on Air and Precipitation Monitoring Networks. Comptes rendus du symposium sur la surveillance et l'évaluation des polluants en suspension dans l'air et notamment sur le transport à grande distance et le dépôt de substances acides et Atelier sur les réseaux de surveillance de l'air et des précipitations. 1983. 502 pp. $8.00.
20643	Interactions of Selenium. 1983. 85 pp. $5.00
20644	Interactions du sélénium avec d'autres éléments. 1983. 85 pp. $5.00
20645	Impact Assessments in Lotic Environments - Methoxychlor. 1983. 130 pp. $5.00
20646	Evaluation des effets du méthoxychlore dans les milieux lotiques. 1984. 144 pp. $5.00
20647	2,4-D: Some Current Issues. 1983. 99 pp. $5.00
20648	2,4-D: quelques questions actuelles. 1984. 106 pp. $5.00

NRCC No. CNRC n°	
22488	TFM and Bayer 73: Lampricides in the Aquatic Environment. 1985. 184 pp. $5.00.
22490	Environmental Aspects of *Escherichia coli* in Human Health. 1984. 76 pp. $5.00.
22491	*Escherichia coli* et la santé humaine - aspects environnementaux. 1985. 71 pp. $5.00.
22492	Post "IBT" Assessment of Critical Laboratory Studies on the Mammalian and Avian Toxicology of Fenitrothion. 1984. 110 pp. $5.00
22493	Évaluation des principles études de laboratoire sur la toxicité du fénitrothion pour les mammifères et les oiseaux réalisée à la suite de "l'affaire IBT". 1984. 114 pp. $5.00
22494	Organotin Compounds in the Aquatic Environment: Scientific Criteria for Assessing Their Effects on Environmental Quality. 1985. 284 pp. $10.00
22844	Exposure of the Hand to Vibration in Industry. 1984. 63 pp. $5.00
22845	Exposition de la main aux vibrations dans le secteur industriel. 1985. 65 pp. $5.00.
22846	Polychlorinated Dibenzofurans: Criteria for Their Effects on Humans and the Environment. 1984. 243 pp. $8.00
22848	Mycotoxins: A Canadian Perspective. 1985. 185 pp. $8.00
23917	Chromium Update 1984: Environmental and Nutritional Effects of Chromium. 1985. 56 pp. $5.00

Available through prepaid purchase orders from

En vente, moyennant commandes prepayées, au Service des

Publications, NRCC/CNRC
Ottawa, Ontario K1A 0R6